



# TITANIUM

With Special Reference to the  
Analysis of Titaniferous Substances

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## GENERAL INTRODUCTION

### American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.



The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie* and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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To  
DOCTOR FRANK AUSTIN GOOCH  
THIS VOLUME IS AFFECTIONATELY DEDICATED



## Preface.

There seems to have been a tendency on the part of the older analysts to regard the presence of titanium in any substance that was being subjected to analysis as something of a nuisance. Indeed, this ill opinion was pretty well justified owing to the inadequacy of the methods then in vogue. Although it must be frankly admitted that titanium in certain of its associations, especially when it accompanies columbium and tantalum, gives rise to very considerable difficulty, and that those procedures that have thus far been proposed as being applicable to such cases leave much to be desired both in point of accuracy and ease of execution; still, with the aid of modern methods, a great variety of naturally occurring materials and technical products, which contain noteworthy amounts of titanium, may be analyzed with all necessary precision and expediency—there being no cause for anxiety as far as the presence of titanium is concerned.

In preparing this work the requirements of the practical analyst have, as far as possible, been kept in mind. Although the attempt has been made to give a complete exposition of the analytical chemistry of titanium, the length at which the various processes have been described varies greatly in different cases, depending partly upon the importance of the process in question and partly upon the amount of available knowledge concerning it. In the case of those methods that have been thoroughly tested and have been found to be reliable, however, an abundance of detail is included; hence the operator should have no difficulty in following them with the inevitable attainment of good results.

Schemes are set forth in Chapter IX for the complete analysis of rutile, ilmenite, ferro-titanium, titanium pigment and titanium-zinc paint (the most important titanium-bearing materials). In other cases the analysis is only partial—in not a few instances the titanium itself being the only constituent whose estimation is provided for, it being of course assumed that with the help of suitable texts on analysis the examination may be extended, if so desired. Moreover, where several alternate procedures are given for the attainment of the same end, the author has endeavored to make the wording such that, under any existing circumstances, a judicious choice of method can be made.

In addition to the analytical part, which indeed makes up the body of the work, it has been thought fit to insert an introductory portion for



the benefit of those who are not familiar with titanium, which gives briefly the circumstances under which it was discovered, its occurrence in nature, a general account of the element and its compounds and finally the industrial applications. In other words, these preliminary chapters are intended to answer such questions as the layman might naturally and rightfully ask. At the same time, it is believed that such an introduction will make more intelligible the principles upon which the analytical processes subsequently described are based.

Finally, a third part has been added, wherein the preparation of certain chemical reagents is described, which have been found to be of special value in the analysis of titaniferous substances, and which are not so readily available in a state of purity.

A somewhat elaborate system of references has been used throughout the text, thus enabling the reader to seek further information on any of the subjects treated from supposedly reliable authorities with all possible convenience to himself. The abbreviations for the names of periodicals are, as far as may be, those sanctioned by the American Chemical Society (anon.: *C. A.*, 16, I-LX (1922)). The names of reference books, however, are given in full along with the name of the publisher; and, in the case of certain foreign books that are not so well known in America, the city in which the press is located is also included.

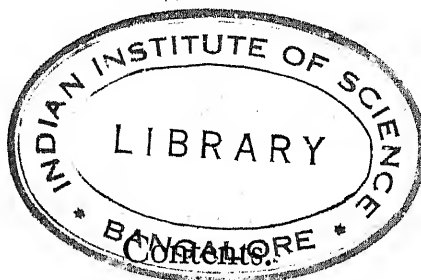
It remains now for the author to acknowledge the very valuable services of those who have contributed so largely toward the completion of this task and to express his sincere thanks for their coöperation. Mr. Frank L. Hess (now with the Bureau of Mines) of the United States Geological Survey made a very careful review of Chapter II, "The Occurrence of Titanium in Nature", and also donated several excellent photographs of titanium minerals. Miss Dorothy Getz, a former assistant in quantitative chemical analysis in the Johns Hopkins University, was very helpful during the early stages of the work—especially in cataloguing the patent literature and writing the first draught of Chapter III, "The General Chemistry of Titanium". Through the courtesy of Mr. L. E. Barton the author was permitted to visit the plants of the Titanium Alloy Manufacturing Company and the Titanium Pigment Company, Inc., at Niagara Falls in the spring of 1924; as the result of which much valuable information was acquired in connection with the industrial chemistry of titanium. Moreover, Mr. Barton made a final criticism of the manuscript (July 13, 1926) paying particularly close attention to the first four chapters. Other gentlemen, each of whom contributed a certain definite amount of help, are: Mr. W. M. Slater of the American Rutile Company, Mr. R. B. Williams of the Metal and Thermit Corporation, Dr. E. R. Berry of the General Electric Company, Prof. F. P. Dunnington of the University of

Virginia and Mr. J. Edward Whitfield of the firm of Booth, Garrett and Blair (analytical and consulting chemists). In like manner, Mr. D. B. Bradner of the Edgewood Arsenal donated a very good photograph of a titanium chloride smoke screen. Finally, the author's former assistants in the Johns Hopkins University, Dr. Paul W. Bachman and Mr. William A. Gerstmyer (especially the latter) made a good many excellent pen and ink drawings, which serve to illustrate some of the more important processes.

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Baltimore, Md.,  
July 24, 1926.





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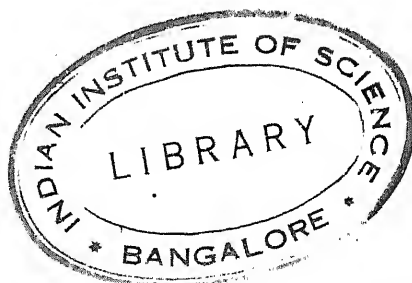
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## PART I.

### INTRODUCTORY.

#### Chapter I.

#### The Discovery of Titanium.

In 1791 W. Gregor,<sup>1</sup> a priest of the parish of Menachan, in Cornwall, England, found in a valley of that parish a black sand, occurring in great abundance, which he described as being much like gunpowder in appearance. He concluded from his examination of this material that the grains were composed of the oxides of iron and a new metal. The sand received the name "menakanite", and the oxide was christened "menakine" by R. Kirwan.<sup>2</sup>

This discovery passed almost unnoticed until 1797. At that time M. H. Klaproth<sup>3</sup> identified the oxide of menakanite with that which he had extracted in 1795 from "red schorl" (rutile) of Boonik, Hungary.<sup>4</sup>

Notwithstanding the priority of Gregor's observations, the name of "titanic earth" (whence titanium), applied by Klaproth in allusion to the "Titans", the fabled giants of ancient mythology, has remained.

## Chapter II.

### The Occurrence of Titanium in Nature.

#### (1) GENERAL DISTRIBUTION.

Although formerly regarded as one of the rare elements, titanium is very widely distributed in the earth's crust; and in such quantity as to make it a relatively abundant substance. According to F. W. Clarke's<sup>1</sup> most recent calculations titanium makes up 0.62 per cent of the lithosphere and 0.58 per cent of known terrestrial matter. Confining our attention then to the solid portion of the globe, titanium stands ninth in order of abundance and next below magnesium. Assuming Clarke's figures to be representative, some rather surprising comparisons may be made. For instance, titanium is nearly one third as plentiful in nature as magnesium, and the ratio of titanium to phosphorus and sulfur is more than five to one and nine to one respectively; in spite of the fact that these three elements are usually considered common. Granting that it be a "rare element", there is certainly more of it in the accessible parts of the earth than there is of all the other "rare elements" put together. Out of 800 igneous rocks analyzed in the laboratory of the United States Geological Survey,<sup>2</sup> 784 contained titanium. While serving as chemist on the Virginia Geological Survey, the author did not fail to obtain a positive test for titanium in a single silicate rock. Regarding its presence in rocks, H. S. Washington<sup>3</sup> writes as follows: "Its amount is very small in the more quartzose and feldspathic rocks but it is most abundant in the more femic rocks". That it probably exists at great depths in the earth's interior is shown by the fact that A. B. Griffiths<sup>4</sup> has observed a noteworthy amount in the volcanic dust of Mont Pelée. It has also been found in the deep sea dredgings of the *Challenger* and similar expeditions.<sup>5</sup> Because of the refractory nature of some of its minerals titanium is often found concentrated in the residual decomposition products of many rocks. Thus F. P. Dunnington<sup>6</sup> has pointed out the wide-spread distribution of titanium in soils and clays, C. Baskerville<sup>7</sup> has noted its presence in peats and C. E. Wait<sup>8</sup> has found astonishingly large amounts in the ashes of certain coals. Titanium is said to be present in some waters. A. Schwager<sup>9</sup> has detected a trace in water from the Danube; though

F. A. Gooch and J. E. Whitfield,<sup>10</sup> on the other hand, have recorded its absence in waters of the Yellowstone National Park. In addition to the above, many forms of organized matter are known to contain titanium. Wait<sup>11</sup> finds very appreciable amounts in the ashes of different kinds of wood, viz., oak, apple and pear, and smaller quantities in the ashes of cow peas and cotton seed meal, and Baskerville<sup>12</sup> notes its presence in the bones and flesh of men and the lower animals. It has been detected in meteorites. J. N. Lockyer<sup>13</sup> states that by means of the spectroscope Thalén discovered titanium in the atmosphere of the sun as early as 1868. In like manner it has been identified in many stars.

The minerals that contain titanium are listed in Table I.

TABLE I.<sup>a</sup>  
TITANIUM MINERALS.

No. <sup>b</sup>	Name	Composition	Per Cent TiO <sub>2</sub>
<i>Oxides (Anhydrous)</i>			
250	Rutile .....	TiO <sub>2</sub>	100
252	Octahedrite (Anatase) ..	TiO <sub>2</sub>	100
253	Brookite .....	TiO <sub>2</sub>	100
237	Magnetite .....	Fe <sub>3</sub> O <sub>4</sub>	Variable
	Baddeleyite <sup>c</sup> .....	ZrO <sub>2</sub>	up to 25
<i>Oxides (Hydrated)</i>			
	Hydrated Titanic Oxide <sup>d</sup> .....	TiO <sub>2</sub> + nH <sub>2</sub> O	.....
261	Bauxite <sup>e</sup> .....	Al <sub>2</sub> O <sub>3</sub> + 2H <sub>2</sub> O	Variable
<i>Titanates</i>			
233	Ilmenite (Menaccanite) ..	FeTiO <sub>3</sub>	52.7
	Pyrophanite .....	MnTiO <sub>3</sub>	53.1
	Geikielite .....	(Mg,Fe)TiO <sub>3</sub>	About 61
518	Perovskite .....	CaTiO <sub>3</sub>	58.9
246	Pseudobrookite .....	Fe <sub>2</sub> (TiO <sub>4</sub> ) <sub>3</sub>	42.9
	Arizonite .....	Fe <sub>2</sub> TiO <sub>5</sub>	58.8
	Knopite .....	RTiO <sub>3</sub> . Related to perovskite but contains cerium.	54.1-58.7
	Iserite .....	FeTi <sub>2</sub> O <sub>7</sub>	69.5
	Yttrocrasite .....	R <sup>II</sup> O. R <sup>IV</sup> O <sub>2</sub> . 3R <sup>III</sup> O <sub>3</sub> . 16TiO <sub>2</sub> + 6H <sub>2</sub> O	49.7
		R <sup>II</sup> = (Ca,Pb,Fe); R <sup>IV</sup> = (Th,U); R <sup>III</sup> = rare earths.	
	Delorenzite .....	2FeO. UO <sub>3</sub> . 2Y <sub>2</sub> O <sub>3</sub> . 24TiO <sub>2</sub> (?)	65.9
<i>Titano-silicates</i>			
510	Titanite (Sphene) ...	CaTiSiO <sub>5</sub>	40.8
371	Schorlomite .....	3CaO. (Fe,Ti) <sub>2</sub> O <sub>3</sub> . 3(Si,Ti)O <sub>2</sub>	12.5-22.1

TABLE I.<sup>a</sup> (Cont.)

No. <sup>b</sup>	Name	Composition	Per Cent TiO <sub>2</sub>
<i>Titano-silicates (Cont.)</i>			
511	Keilhauite .....	15CaTiSiO <sub>5</sub> . (Al,Fe,Y) <sub>2</sub> (Si,Ti)O <sub>5</sub>	26.7-36.6
513	Tscheffkinit <sup>c</sup> .....	(Fe,Ca) <sub>3</sub> Ce <sub>2</sub> Ti <sub>4</sub> Si <sub>6</sub> O <sub>22</sub>	16.1-21.2
514	Astrophyllite .....	R <sup>I</sup> R <sup>II</sup> Ti(SiO <sub>4</sub> ) <sub>4</sub> R <sup>I</sup> = (H,Na,K); R <sup>II</sup> = (Fe,Mn)	7.1-13.6
343	Ænigmatite .....	2Na <sub>2</sub> O.9FeO.AlFeO <sub>3</sub> .12(Si,Ti)O <sub>2</sub>	5.6
343	Cossyrite .....	See Ænigmatite.	
511	Yttrotitanite .....	See Keilhauite.	
	Lamprophyllite .....	Related to Astrophyllite.	
	Neptunite .....	R <sub>2</sub> IR <sup>II</sup> TiSi <sub>4</sub> O <sub>12</sub> R <sup>I</sup> = (Na,K); R <sup>II</sup> = (Fe,Mn)	18.1
515	Johnstrupite .....	Complex.	
516	Mosandrite .....	See Johnstrupite.	
517	Rinkite .....	(Fe <sub>3</sub> Ti <sub>4</sub> )Na <sub>2</sub> Ca <sub>11</sub> Ce <sub>3</sub> (SiO <sub>4</sub> ) <sub>12</sub> (?) Cf. Johnstrupite and Mosandrite.	13.4
371	Ivaarite .....	See Schorlomite.	19.0
	Carlosite .....	See Neptunite.	
	Benitoite <sup>c</sup> .....	BaTiSi <sub>3</sub> O <sub>9</sub>	19.3
	Lorenzenite .....	Na <sub>2</sub> (TiO) <sub>3</sub> Si <sub>3</sub> O <sub>7</sub>	35.1
	Davidite .....	Uncertain.	50.0+
	Narsarsukite .....	Complex.	14.0
<i>Columbates and Tantalates</i>			
520	Pyrochlore .....	RCb <sub>2</sub> O <sub>6</sub> .R(Ti,Th)O <sub>3</sub> .NaF R = Ce metals, Ca and other bases.	5.4-13.6
532	Æschynite .....	2Y(CbO <sub>3</sub> ) <sub>3</sub> .2ThTiO <sub>4</sub> .3TiO <sub>2</sub>	21.2
533	Polymignite .....	5RTiO <sub>3</sub> .5RZrO <sub>3</sub> .R(Cb,Ta) <sub>2</sub> O <sub>6</sub> R = Ce metals, Fe and Ca.	18.9
534	Euxenite .....	R <sup>III</sup> (CbO <sub>3</sub> ) <sub>3</sub> .R <sub>2</sub> <sup>III</sup> (TiO <sub>3</sub> ) <sub>3</sub> +3/2H <sub>2</sub> O R <sup>III</sup> = Y, Er, Ce and U.	20-35
535	Polycrase .....	R <sup>III</sup> (CbO <sub>3</sub> ) <sub>3</sub> .2R <sub>2</sub> <sup>III</sup> (TiO <sub>3</sub> ) <sub>3</sub> +3H <sub>2</sub> O R <sup>III</sup> = Y, Er, Ce and U.	25.2-29.3
	Blomstrandite .....	Complex.	10.7
519	Dysanalyte .....	6RTiO <sub>3</sub> .RCb <sub>2</sub> O <sub>6</sub> R = Ca and Fe.	40.6-59.3
	Strüverite <sup>b</sup> .....	FeO.(Ta,Cb) <sub>2</sub> O <sub>6</sub> .6TiO <sub>2</sub> (?)	49
	Epistolite .....	Uncertain.	7.2
	Blomstrandine-Priorite.	Complex.	22-33
	Ilmenorutile .....	FeO.Cb <sub>2</sub> O <sub>6</sub> .5TiO <sub>2</sub> (?) Cf. Strüverite.	53-74
<i>Silicates</i>			
334	Amphibole .....	Complex.	Variable up to 8.5
325	Pyroxene .....	Complex.	Variable up to 4.6
462	Biotite .....	Complex.	Variable up to 4.7
462B	Lepidomelane .....	Complex. Cf. Biotite.	Ditto

TABLE I.<sup>a</sup> (Cont.)

No. <sup>b</sup>	Name	Composition	Per Cent TiO <sub>2</sub>
<i>Silicates (Cont.)</i>			
331	Rosenbuschite .....	6CaSiO <sub>3</sub> .2Na <sub>2</sub> ZrO <sub>2</sub> F <sub>2</sub> . (TiSiO <sub>3</sub> , TiO <sub>3</sub> )	6.8-7.6
376B	Titanolivine .....	(Mg,Fe) <sub>2</sub> SiO <sub>4</sub>	3.5-6.1
370	Garnet (var. Andradite) .....	Ca <sub>3</sub> Fe <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	Variable up to 10.8
394	Zircon <sup>c</sup> .....	ZrSiO <sub>4</sub>	Variable
	Leucosphenite .....	Na <sub>4</sub> Ba(TiO) <sub>2</sub> (Si <sub>2</sub> O <sub>6</sub> ) <sub>3</sub>	13.2
	Rhonite .....	Complex.	9.5
		Cf. Ænigmatite.	
<i>Miscellaneous</i>			
700	Hydrotitanite .....	Altered form of Dysanolyte.	82.8
	Warwickite <sup>d</sup> .....	(Mg,Fe) <sub>2</sub> TiB <sub>2</sub> O <sub>8</sub>	27.9
	Zirkelite .....	(Ca,Fe)(Zr,Ti,Th) <sub>2</sub> O <sub>8</sub>	14.9
	Derbylite .....	6FeO.TiO <sub>2</sub> .Sb <sub>2</sub> O <sub>5</sub> (?)	34.6
	Lewisite .....	5CaO.2TiO <sub>2</sub> .3Sb <sub>2</sub> O <sub>5</sub>	11.7
	Mauzeilite .....	4(Ca,Pb)O.TiO <sub>2</sub> .2Sb <sub>2</sub> O <sub>5</sub>	7.9
		Cf. Lewisite.	
	Hainite .....	Uncertain.	....
		Cf. Mosandrite.	
	Senaite .....	(Fe,Pb)O.2(Ti,Mn)O <sub>2</sub> (?)	57.2

<sup>a</sup> Modelled after a similar table by Watson and Taber: Va. Geol. Survey, Bull. III-A, 10 (1913).

<sup>b</sup> Numbers refer to Dana: System of Mineralogy, 1909. John Wiley & Sons, Inc.

<sup>c</sup> Brown: J. Am. Chem. Soc., 39, 2358 (1917).

<sup>d</sup> Gorceix: Bull. soc. min., 7, 179 (1884).

<sup>e</sup> Anderson: Bur. Mines, Reports of Investigations, Ser. No. 2406, 5 (1922).

<sup>f</sup> Clarke: U. S. Geol. Survey, Bull. 588, 122 (1914).

<sup>g</sup> Louderback: Bull. Dept. Geol. Univ. Calif., 5, 149 (1907); 5, 331 (1909).

<sup>h</sup> Hess and Wells: Am. J. Sci., (4), 31, 432 (1911).

<sup>i</sup> Bradley: ibid. (4), 27, 179 (1909).

In spite of the fact that titanium occurs, either as an essential or as an accidental ingredient, in a large number of minerals, there are at present only two distinct species which are of economic importance, viz., rutile and ilmenite. Though most mineralogists are of the opinion that titaniferous iron ores are composed primarily of magnetite (and more rarely hematite) with intergrowths of ilmenite, at least one authority, viz., J. T. Singewald, Jr.,<sup>14</sup> holds that titanium may be present as an integral part of the magnetite molecule itself. In view of this uncertainty, it seems well to tentatively include magnetite as a notable titanium bearing substance. Accordingly the three minerals, rutile, ilmenite and magnetite, will be described in some detail.

## (2) DESCRIPTION OF THE MINERALS.

## Rutile.

*Composition.* Rutile is titanium dioxide, or titanic oxide ( $\text{TiO}_2$ ), containing theoretically 40.05 per cent of oxygen and 59.95 per cent of titanium. Iron is usually present—sometimes in large amount. Some rutiles are stanniferous, and many contain small but determinable quantities of both chromium and vanadium.<sup>15</sup> A very common impurity is silicon dioxide, which probably exists as admixed quartz or some silicate mineral; while certain other elements, notably manganese, have been detected in small amounts. Rutile is normally anhydrous, though a hydrated variety of titanic oxide is known (see Table I). The finely powdered material shows no greater moisture content than that attributable to the hygroscopicity of any substance in small particles.

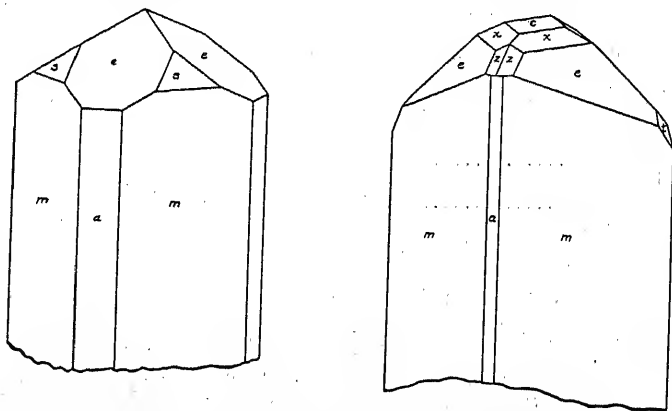


FIG. 1.—Rutile (left) and brookite (right.)

(Letters denoting crystal forms are identical with those in Dana: *System of Mineralogy*, 1909, pp. 237 and 242. John Wiley & Sons, Inc.)

*Crystallization.* Tetragonal. Axis  $c = 0.644$ . Angle  $s \wedge s = 56^\circ 52'$  and  $c \wedge s = 42^\circ 20'$  ( $c$  denoting the basal pinacoid—not present on crystal of Figure 1). The crystals are usually prismatic and often capillary. Prisms of the first and second orders,  $m(110)$  and  $a(100)$ , and terminating pyramids of the first and second orders,  $s(111)$  and  $e(101)$ , are common forms. Twin crystals are of frequent occurrence, the pyramid of the second order being the twinning-plane. Often a network of prisms, crossing at angles of nearly  $60^\circ$  and  $120^\circ$ , and zigzag groups are the results of repeated twinning. Rather recently, F. L. Hess<sup>16</sup> observed microscopic rutile crystals radiating from a common center in a float specimen from Custer, South Dakota. (See

photomicrograph of Figure 2.) Finally, rutile crystals are characterized by vertical striations on the prism faces.

The polymorphism of titanic oxide, as exhibited in nature by the minerals rutile (tetragonal) and brookite (orthorhombic), is shown by



(Courtesy of Mr. Frank L. Hess of the U. S. Geological Survey.)

FIG. 2.—Radial rutile crystals. A float specimen from Custer, S. Dak. Magnified 85 diameters. From Warren R. Bond, Custer, S. Dak.

the crystal drawings of Figure 1. Still another form is the mineral octahedrite,<sup>17</sup> which is tetragonal though not derivable from rutile.<sup>18</sup>

*Structure.* Rutile is usually crystallized; though compact masses, displaying no outward signs of crystallization, are common. Cleavage



parallel to the prism faces a and m is distinct; but along the pyramid s it is much less marked.

Hair-like crystals penetrating clear quartz constitute the stone known as "flèches d'amour", "Venus hair-stone", etc.

*Physical Properties.* Rutile has a hardness of 6-6.5 on the Mohs scale (between orthoclase and quartz) and a specific gravity varying from 4.18 to 4.25. The luster is adamantine to submetallic. The color is generally reddish brown; but deep red transparent specimens are to be found on the one hand and black opaque varieties on the other. A grass-green variety is also known, which contains chromium. The streak is pale brown or colorless.

*Tests.* Rutile is infusible before the blowpipe (melting point above  $1300^{\circ}\text{C}.$ ). The fine powder dissolves slowly in the microcosmic salt bead under the influence of the oxidizing flame and the color of the resulting globule is yellow; but on applying a strong reducing flame the color changes gradually to violet. No matter how finely comminuted the mineral does not dissolve completely in any acid nor in any mixture of acids. On fusing with sodium carbonate and extracting with strong hydrochloric acid, the titanium goes into solution. The addition of granulated tin or zinc, warming if necessary, gives rise to a beautiful amethystine color. A more delicate test for titanium in minerals depends upon fusing the substance in excessively fine powder with a large excess of potassium pyrosulfate in a covered platinum crucible. After dissolving the cold melt in sulfuric acid (10 per cent by volume) without warming and adding hydrogen peroxide, an intense orange color will make its appearance. Other reactions are described in Chapter III (5).

*Occurrence.* Rutile is found in igneous, metamorphic and sedimentary rocks—either as an accessory mineral in the rock or in quartz veins traversing it. It is sometimes a pyrogenetic constituent of igneous rocks and sometimes an alteration product derived from ilmenite and titanite and perhaps other titaniferous minerals. It is an exceedingly stable material and is therefore found concentrated in sand beds. Among its common associates are quartz, feldspar, ilmenite, hematite, etc.

### Ilmenite.

*Composition.* The chemical composition of ilmenite<sup>19</sup> has been a matter of considerable discussion. It was formerly regarded as iron titanium sesquioxide,  $(\text{Fe}, \text{Ti})_2\text{O}_3$ , isomorphous with hematite,  $\text{Fe}_2\text{O}_3$ ; but it is now generally thought to be ferrous titanate,  $\text{FeTiO}_3$ , isomorphous with pyrophanite,  $\text{MnTiO}_3$ , and geikielite,  $\text{MgTiO}_3$ . However, most analyses do not show the mineral to be of definite constitution.

Since the iron is nearly always present in both conditions of valence, the formula  $m\text{FeTiO}_3 \cdot n\text{Fe}_2\text{O}_3$  is used for expressing its composition in a general way. In some specimens, however, the titanite oxide is even in molecular excess of all the iron oxide (calculated as  $\text{FeO}$ ).<sup>20</sup> Magnesium frequently replaces a part of the ferrous iron and the same is true of manganese and calcium to a lesser extent. Silicon dioxide is nearly always present. Some samples contain aluminum. Chromium, vanadium, phosphorus, nickel and tin are likely to occur in small amounts. The water content on unaltered material is very small showing that the mineral is not hydrated.

*Crystallization.* Hexagonal-rhombohedral. Ilmenite belongs to the trirhombohedral group, of which phenacite may be regarded as the type. It thus differs crystallographically from hematite, which is a member of the normal group (calcite type); although the two species are much alike in appearance, and the values of corresponding angles show but little deviation. Good crystals are rather rare. These are usually thick tabular with prominent basal planes and small rhombohedral truncations; the third order rhombohedron is generally missing.

*Structure.* Ilmenite is usually found massive, showing a conchoidal fracture; also as embedded grains in the rock and loose in sand. Thin plates are also common.

*Physical Properties.* The hardness of ilmenite varies from 5.5 to 6, and the specific gravity from 4.5 to 5.0. The color is iron-black, the luster is metallic to submetallic and the streak is black to brownish red.

*Tests.* Ilmenite is infusible before the blowpipe. It is slightly magnetic in its natural state; but is rendered decidedly so when the powder is fused with sodium carbonate in the reducing flame. It dissolves with great difficulty in hydrochloric acid; but is readily soluble in a mixture of hydrofluoric and sulfuric acids—likewise in hydrofluoric and hydrochloric acids. It gives the reactions for titanium in much the same way as rutile.

*Occurrence.* Ilmenite is widely diffused in nature, and occurs as beds and lenticular bodies, sometimes of immense size, in crystalline rocks—also as a common accessory mineral in various igneous and metamorphic rocks. Like rutile it is slow to weather and therefore makes up a noteworthy amount of many sands. Its most common associate is magnetite.

### Magnetite.

*Composition.* Magnetite is an oxide of iron,  $\text{Fe}_3\text{O}_4$ , which if pure would contain 27.6 per cent of oxygen and 72.4 per cent of iron. Titaniferous varieties carry varying though sometimes large amounts



of titanium. The chemical composition of titanium-bearing magnetite, qualitatively speaking, is very much like that of ilmenite.

*Crystallization.* Isometric. Magnetite is strongly octahedral in habit. The dodecahedron appears at times—either alone or in combination with the octahedron.<sup>21</sup> Twinned octahedrons are not uncommon. Octahedral parting is often highly developed.

*Structure.* This well known mineral is generally granular massive, either coarse or fine. Well formed crystals are to be had from various localities.

*Physical Properties.* The hardness of magnetite is about 6, and the specific gravity 5.18. The luster is metallic, color iron-black and streak black. It is strongly attracted by the magnet, and some specimens, known as "lodestone", show distinct polarity.

*Tests.* Magnetite is infusible before the blowpipe; but on being heated in the oxidizing flame it becomes non-magnetic. It dissolves slowly in hot concentrated hydrochloric acid and readily in a mixture of hydrofluoric and sulfuric acids. The solution (free from fluorine for the peroxide test) exhibits the titanium reactions more or less markedly according to the amount of titanium present.

*Occurrence.* Magnetite, being found here and there in large bodies, constitutes an important ore of iron. Magmatic differentiation is thought to be the chief cause of its concentration. It is apt to be associated with rocks rich in ferromagnesian minerals. It is very resistant to weathering and is consequently an abundant component of "black sand". Hematite, ilmenite, corundum and spinel are among its intimate associates.

### (3) TITANIUM ORES.

#### Rutile.

Although the known workable deposits of rutile are rather limited, there are several that have yielded at least some material for commercial purposes. The localities are Roseland, Virginia, and Pablo Beach, Florida, in the United States; Baie St. Paul, Quebec, in Canada; Kragerö in Norway; Madagascar; Queensland and South Australia. As far as is at present known, it may be said that in the Virginia area is the most extensive deposit of rutile in the world.<sup>22</sup>

The Virginia rutile occurs as segregations in a syenite, which in its turn has been intruded into the country rock (gneiss). Other igneous rock types, viz., gabbro, nelsonite, and diabase, are associated with the syenite—usually traversing it in well defined dikes. The syenite shows a long and narrow outline at the surface and has a total area of about 20 square miles, partly in Nelson and partly in Amherst counties. It

is composed chiefly of feldspar and blue quartz; but contains in places, especially near the border, pyroxene (largely altered to hornblende), rutile, ilmenite and apatite. At the American Rutile Company's mine, situated at Roseland on the Tye River, rutile makes up a very noteworthy portion of the syenite (Figure 3); so much so in fact that it has been profitably quarried since 1900. Ilmenite accompanies the rutile in about equal quantity. The rock is crushed to the size of coarse sand,



FIG. 3.—Polished specimen of rutile-bearing syenite (American Rutile Company's ore). The rutile is best seen as dark areas in white feldspar, but it is scattered throughout the mass. Some ilmenite is present also. The dark gray areas represent greenish-gray hornblende and the light gray blue quartz.

and the rutile and ilmenite are concentrated on shaking tables. After drying, the concentrates are passed through a Wetherill magnetic separator, which removes the ilmenite. The remaining rutile carries 95 to 96 per cent of titanium dioxide, and the ilmenite about 54 per cent.<sup>23</sup>

The Florida deposit, which has been described by D. M. Liddell,<sup>24</sup> consists of a complex beach sand, concentrated between low and high tides. It has been worked, mostly for ilmenite, by Buckman and Pritchard, Inc.<sup>25</sup> Four valuable minerals, ilmenite, monazite, zircon and rutile, are obtained on concentration.

Near the village of St. Urbain, about 10 miles north of Baie St. Paul in Quebec, rutile accompanied by sapphirine and other minerals

is enclosed in granular masses of ilmenite, which have been intruded into anorthosite.<sup>26</sup> The amount of rutile varies greatly, being estimated to make up from 0 to 20 per cent of the mass. Rutile-free ilmenite bodies are also found in this locality; and indeed these are in the majority. The St. Urbain deposits have been worked to some extent. The General Electric Company is said to have taken out a considerable quantity of ore in 1910, and a good deal of ilmenite was formerly shipped to Niagara Falls, N. Y. for the manufacture of ferrotitanium.

A very noteworthy occurrence of rutile is that at Kragerö, Norway. Until a few years ago these deposits supplied practically all of the world's rutile. The geology has been studied by W. C. Brögger.<sup>27</sup> "The rutile is accompanied by a moderately acid plagioclase, forming a rock which Brögger terms 'krageröite' and which generally contains 10-15 per cent of rutile. It occurs streak-like in foliated granite in the neighborhood of an enormous dike of granite-pegmatite on one side, and of olivine-hyperite with amphibolite on the other, both of which are traversed by apatite-rutile veins".<sup>28</sup> The Kragerö rutile is unusually rich in chromium and vanadium<sup>29</sup>—a fact which may possibly enhance its economic value.<sup>30</sup>

A. Lacroix<sup>31</sup> reports that rutile occurs in Madagascar in some abundance. It is found more particularly in the mica-schists to the west of Ambatofinandrahana (north of the Matsiatra river), where it exists as large crystals in place. It also occurs loose, but only in small quantity. This material was mined during the recent war for military and naval purposes, as much as 200 metric tons of titanite chloride having been manufactured.

Rutile has been unsystematically mined in both Queensland and South Australia. A deposit 6 miles north of Blumberg has been briefly described by L. C. E. Gee.<sup>32</sup> The rock containing this rutile seems to be of pegmatitic character, though the presence of sillimanite in some specimens would indicate contact metamorphism—at least in places.<sup>33</sup>

Several other rutile localities might be mentioned; but their commercial status at the present time does not warrant any detailed discussion. For instance, rutile was formerly obtained in Chester County, Pennsylvania by hand picking and sold for museum cabinets and to the dental trade. Fine crystals of rutile (along with brookite and octahedrite) have come from Magnet Cove, Arkansas, and some rutile from Graves Mountain, Georgia. Hess<sup>34</sup> announced the existence of a promising area in Goochland and Hanover counties in Virginia. Moreover, two new prospects have recently come to the authors' attention, the one being a rutile-bearing amphibolite at Custer, South Dakota (Figure 5) and the other a deposit at Sonora, Mexico.<sup>35</sup>

## Ilmenite.

The deposits of ilmenite that are of practical interest may be conveniently divided into two classes, viz., those in which the mineral occurs *in situ* and those in which it is found as sand. The ilmenite, obtained from the rock by the American Rutile Company at Roseland, Virginia, has already been mentioned (p. 31). Since ilmenite and



(Courtesy of Mr. Frank L. Hess of the U. S. Geological Survey.)

FIG. 4.—Specimen of rutile-bearing vein (rutile-nelsonite) from General Electric Company's prospect near Arrington, Nelson Co., Va. The mass is composed essentially of rutile (dark) and apatite (light).

magnetite are so intimately associated in nature—the percentage of titanic oxide in titaniferous magnetites ranging all the way from 45 down to 2 or even less—it seems best to reserve the discussion of massive ores for the next section, "Titaniferous Iron Ores".

Certain monazite sands, notably those along the coast of Bahia, Brazil, constitute a large potential supply of ilmenite, whence it may be obtained as a by-product in the concentration of the monazite. These



(Courtesy of Mr. Frank L. Hess of the U. S. Geological Survey.)

FIG. 5.—Rutile (black crystals) in actinolite. From an amphibolite dike, Custer, S. Dak. Magnified 48 diameters. From Warren R. Bond, Custer, S. Dak.

concentrates run very high in titanium, the Brazilian being of theoretical richness (52.7 per cent titanium oxide). A similar occurrence in this country is the Pablo Beach deposit in Florida (p. 31), which too yields an ilmenite concentrate of something like 52 per cent.<sup>86</sup> In fact the placer mining of ilmenite in connection with other valuable minerals (especially monazite) has been found so simple and inexpensive that outside of Norway the massive titaniferous ores are not being worked to any great extent at present.<sup>87</sup>

Another possible source of titanium is the peculiar rock type, which T. L. Watson<sup>88</sup> has designated "nelsonite", occurring in the Amherst-



Nelson counties region of Virginia and in Roanoke County also to some extent. In the former area narrow well defined dikes of igneous origin have been intruded chiefly into the syenite (p. 30) and to a lesser degree into the surrounding gneiss near the contact. Watson and Taber<sup>39</sup> distinguish six varieties of nelsonite; but only two need be considered in this connection, viz., ilmenite-nelsonite and rutile-nelsonite—the former being essentially an ilmenite apatite mixture and the latter a rutile apatite mixture (Figure 4). These mineral aggregates have tempted the prospector; since not only would the titanium compounds be of value but the calcium phosphate could be used for fertilizer as well. However, nelsonite has not yet been commercially utilized for several reasons, which have been clearly set forth by Watson and Taber,<sup>40</sup> to whom the reader is referred for further discussion. It should be noted, however, that a small amount of apatite remaining in the concentrated titanium minerals would not vitiate them for the manufacture of pigment to anything like the same extent as for use in iron and steel metallurgy; hence the future utilization of the nelsonite ores is more promising now than formerly, as the pigment industry has become the more important of the two. (See Chapter IV, p. 65.)

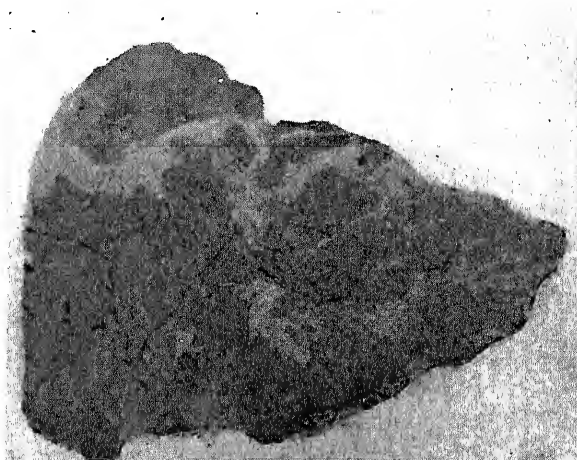
### Titaniferous Iron Ores.

The term "titaniferous iron ore" might be logically taken to mean any ore of iron that contains a noteworthy amount of titanium. As a matter of usage, however, the phrase is generally employed in a more restricted sense, denoting a titanium-bearing magnetite. Nevertheless, it should be added that certain ore bodies, such as those at St. Urbain, Quebec, and at Egersund, Norway, are known, which consist of well-defined crystallographic intergrowths of ilmenite and hematite. Regarding the more usual type then, it may be said that the titanium is present in the ores as ilmenite grains, inclusions and intergrowths of ilmenite in the magnetite and, in Singewald's<sup>41</sup> opinion, in the magnetite molecule itself. As previously noted (p. 34), the ratio of ilmenite to magnetite varies greatly so that there is really no sharp distinction between ordinary magnetite and titaniferous magnetite on the one hand nor between titaniferous magnetite and ilmenite on the other. These ore bodies, which are associated with basic rocks like anorthosite, gabbo, pyroxenite, etc., are thought to be the results of magmatic differentiation; though Singewald<sup>42</sup> has observed a case of contact metamorphism in the Cebolla district of Colorado. The ores occur rather abundantly in at least four countries, Norway, Madagascar, Canada and the United States. Other deposits are known, e.g., those in northern Sweden and of Taberg in southern Sweden, in the Ilmen Mountains of Russia, near



Olary in South Australia, etc. . . . ; but judging from present developments they are comparatively unimportant.

Although titanium-bearing ore is found at several places in Norway, the most important locality is the vicinity of Egersund. Here two deposits, Laxedals and Blaafjeldet, are being mined by the Titan Company A/S of Fredrikstad, Norway—chiefly for the manufacture of titanium pigment. The Blaafjeldet, carrying between 40 and 45 per cent of titanium oxide, is not only richer but of far greater extent than the Laxedals, which carries about 35 per cent—being estimated



(Courtesy of Mr. Frank L. Hess of the U. S. Geological Survey.)

FIG. 6.—Ilmenite in gneiss from Carmen P. O. (Alleghany), Madison Co., N. C.

at 30,000,000 metric tons to 100 meters in depth as compared with 250,000 tons.<sup>43</sup>

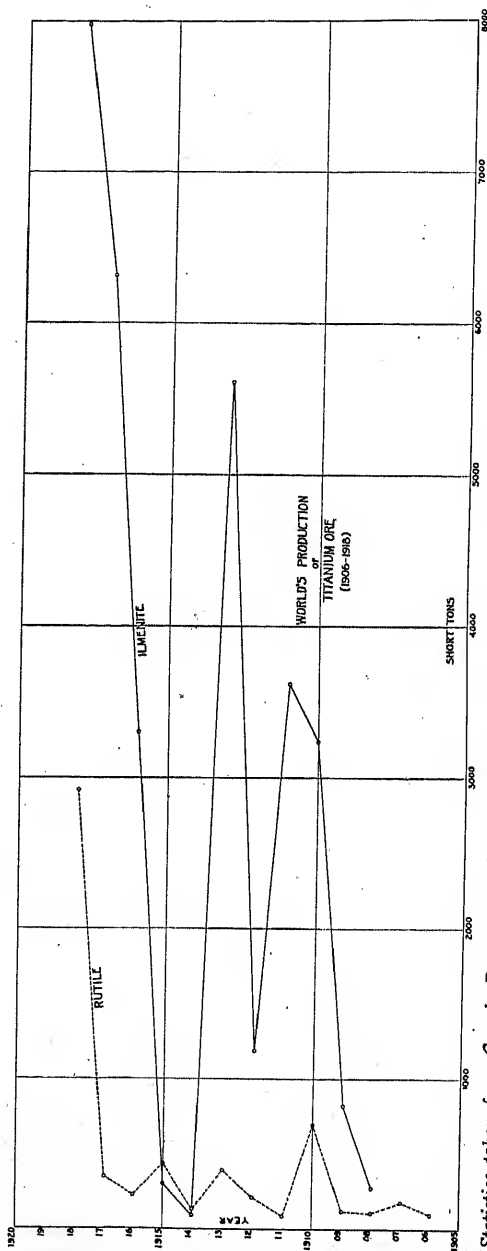
Titanic iron ore is said to occur in Madagascar in very considerable quantity. Lacroix<sup>44</sup> states that there are two types of ore on the island: the one being an intimate admixture of ilmenite and hematite enclosed by gneiss and located not far from Betroka and the other an ilmenite magnetite mixture derived from gabbro and occurring in the valley of the Vongoa river (a tributary of the Mahajilo). The former contains 27 per cent of titanium oxide, but for the latter no valuation is given.

The important ores of Canada are confined to the provinces of Quebec and Ontario. According to A. H. A. Robinson<sup>45</sup> the deposits are five in number, viz., ilmenite at St. Urbain (p. 31) and at Ivry at Quebec, titaniferous magnetite on the Saguenay river, near lake St. John, Quebec, at Bay of Seven Islands, also in Quebec, and an extensive series running along the shores of Seine bay and Bad Vermillion

lake in western Ontario. The Canadian titanium resources compare favorably with those of other parts of the world.<sup>46</sup>

In the United States titaniferous iron ores occur in Rhode Island, New York, New Jersey, North Carolina, Minnesota, Wyoming and Colorado. The only two deposits that offer much economic promise are those at Sanford Hill in the Adirondack mountains of New York and at Iron Mountain, Wyoming. The others are either of too small extent or the ores are too lean.<sup>47</sup>

The commercial utilization of the titaniferous iron ores has long been a matter of debate. In years past it was thought that such materials could not be used for the production of iron owing to the formation of titanate-containing slags of high viscosity that would inevitably clog up the blast furnace. More recent experiments, notably those of A. J. Rossi,<sup>48</sup> F. E. Bachman<sup>49</sup> and a few other investigators,<sup>50</sup> have demonstrated the fact that, when the ores are properly fluxed and when suitable conditions of temperature and blast pressure are maintained, titaniferous ores can be successfully smelted in the blast furnace and will yield iron of excellent quality. Whether or not these favorable results may be expected in the case of the blast furnace of present day construction probably depends upon the amount of titanium carried by the ore. In the older furnace, operating at not too high a temperature, the titanium went almost entirely into the slag. With the more modern type of furnace, however, operating under higher pressure and consequently at a higher temperature, it seems probable that certain difficultly fusible "semi-metallic" products (such as nitride and cyanonitride of titanium) would form and that these, if excessive, would tend to give trouble. However, the researches of Bachman<sup>51</sup> have shown that a considerable amount of titanium can be carried without difficulty; and it would seem that titaniferous ores could be successfully handled in the modern blast furnace if they were mixed with non-titaniferous ore in such proportion that the titanium compounds formed could be readily removed with the slag.<sup>52</sup> The direct production of steel by smelting titanic iron ores in the electric furnace, wherein the titanium can be made to enter either the metal or the slag by controlling the temperature, has been shown to be feasible; but it does not seem that these ores would have any advantage over non-titaniferous ores under similar treatment.<sup>53</sup> But this is only one phase of the question. The increasing demand for titanium leads one to believe that the future working of these ores will not be by such methods as will totally waste their titanium content. Two different procedures have been suggested for making both the iron and the titanium available, viz., magnetic separation and the electric furnace concentration process of Rossi.<sup>54</sup> Different ores do not lend themselves to magnetic parting equally well, as Singewald<sup>55</sup> has pointed



(Statistics taken from Canada Department of Mines, Mines Branch, No. 579, p. 93, 1922.)  
 FIG. 7.—World's production of titanium ore (1906-18).

out; though good results have been obtained in certain cases. Nothing is known to the author regarding the workableness of Rossi's idea. All things being considered, it would seem that the titaniferous iron ores, the sum total of which is in all probability very large, will, as time goes on, be much more extensively utilized than they are at present either for the extraction of iron or titanium or both—and possibly for vanadium as well.<sup>56</sup>

#### (4) PRODUCTION AND PRICE.

Prior to 1903, Norway was the only country producing titanium minerals in considerable quantity. With the opening up of the Virginia deposits, the United States gradually became a serious competitor so that by 1909 its output had surpassed that of Norway. This continued until 1918, when a sudden increase in the Norwegian production again put that country in the lead.

Judging from available figures now at hand, Norway reached its maximum production in 1919 of 4,269 metric tons.<sup>57</sup>

Canada has put out a good deal of ilmenite (as much as 6,330 short tons in 1918) but apparently very little rutile.

For 1910 the United States showed a production of 566 short tons of rutile; but this is unusually high, being about double that for 1920. Ilmenite from domestic sources reached 1,644 short tons in 1918; but there has been a decided falling off since then, only 268 short tons in 1920. Indeed, Hess<sup>58</sup> reports that there were no titanium minerals produced in the United States during the year 1921. In 1922, however, 4,581 short tons of ilmenite were obtained from the Florida sands. During the same year, the American Rutile Company<sup>59</sup> produced both rutile and ilmenite at Roseland, Virginia; but figures are not available for publication.

For further statistics on the titanium ores, see Robinson.<sup>60</sup> The world's production of rutile and ilmenite from 1906 to 1918 inclusive is shown graphically in Figure 7.

Market quotations<sup>61</sup> for rutile and ilmenite concentrates on June 19, 1926 are as follows:

*Rutile.* Virginia, per lb.; granular, 94 @ 96 per cent  $\text{TiO}_2$ , 12 @ 15¢; pulverized, 100-mesh, 94 @ 96 per cent, 17 @ 30¢.

Ditto—Florida, 93 per cent  $\text{TiO}_2$ , \$200 per ton.

*Ilmenite.* Concentrates, 52 per cent  $\text{TiO}_2$ , 1½¢ per lb., f.o.b. Virginia points.

Ditto—\$60 per short ton, Florida mines.

## Chapter III.

### The General Chemistry of Titanium.

#### (1) CHEMICAL RELATIONS OF THE ELEMENT.

According to Mendeléeff's periodic system of the elements, titanium is found in the carbon group together with those elements that show a characteristic valence of four (Figure 8). As is usually the case with the first member of a group, carbon possesses certain unique properties. Silicon resembles germanium a little more closely than does titanium, and so may be classed in family B with carbon, germanium, tin and lead. Titanium, on the other hand, is the first member of family A, which also includes zirconium, cerium, perhaps the newly discovered element hafnium (element No. 72)<sup>1</sup> and thorium. However, the difference between the families in this part of the table is not so very marked; though the elements in A are somewhat more electropositive than those similarly placed in B.<sup>2</sup> In the comparison of the members of Group IV A, cerium may be disregarded because of its resemblance to the rare earths—it being doubtless more logical to treat the latter elements in a group by themselves.

In the quadrivalent state titanium forms salts which are readily hydrolyzed. The analogous zirconium salts are hydrolyzed with greater difficulty than those of titanium. Finally, the thorium salts are decidedly more stable than those of zirconium. The increase in metallic character, in going from titanium to thorium, may be shown in other ways. For instance, though all three elements form oxides of the type  $\text{XO}_2$ ,  $\text{TiO}_2$  is amphoteric, acidic properties end with  $\text{ZrO}_2$  and  $\text{ThO}_2$  is basic only. With the exception of carbon, alkali salts of  $\text{H}_2\text{XF}_6$  are typical compounds of the entire fourth group. Furthermore, members of Group IV A form peroxides which distinguish these elements from those in Group IV B, and connect them with preceding A subgroups; since lanthanum forms a peroxide as do the alkaline earths and alkalis. Again, by virtue of its variable valence, titanium is connected with the polyvalent elements following it to the right. There are alums of trivalent titanium, which show its similarity to vanadium, chromium, manganese and iron. It forms bivalent compounds also, again resembling the elements just mentioned. Some chemists have claimed

a yet higher valence for titanium,<sup>8</sup> whereas others deny the probability of it having a valence higher than four<sup>4</sup>—the question having arisen because of the existence of pertitanic acid and the pertitanic salts, concerning which more will be said in (4).

			MENDELEEFF'S PERIODIC SYS					
GROUP			III		IV		V	
TYPE FORMULA			R <sub>2</sub> O <sub>3</sub>		RO <sub>2</sub>		RH <sub>5</sub>	
FAMILY			A	B	A	B	A	B
PERIOD	SERIES							
	0							
	1							
1	2		B = 108		C = 12		N = 14	
2	3		Al = 27		Si = 28		P = 31	
3	4		Sc = 45.1		Ti = 47.9		V = 51	
	5		Ga = 70.1		Ge = 72.5		As = 75	
4	6		Yt = 89.3		Zr = 90.6		Nb = 93.1	
	7		In = 114.8		Sn = 118.7		Sb = 120.3	
5	8		La = 139		Ce = 140.25			
	9							
6	10						Te = 128.15	
	11		Tl = 204		Pb = 207.2		Bi = 209	
7	12		Ac = 230?		Th = 232.15			

FIG. 8.—Section of D. J. Mendeléeff's periodic table.

## (2) THE ATOMIC WEIGHT OF TITANIUM.

The atomic weight of titanium was determined as early as 1823 by H. Rose,<sup>5</sup> who attempted to convert the disulfide into the dioxide by heating it in a current of air; but the results were unsatisfactory. In 1829 the same investigator obtained more concordant values by working with the tetrachloride.<sup>6</sup> G. Mosander,<sup>7</sup> I. Pierre<sup>8</sup> and A. Demarcay<sup>9</sup> each in his turn, contributed a determination of this quantity. This early work, however, may be dismissed as being of historical interest only.<sup>10</sup>

The 1922 International value, 48.1, is based on the work of Thorpe,<sup>11</sup> who carried out six series of experiments, the temperature being 0°C. This is a some-

chloride and three with the bromide, involving thirty-one determinations in all. Using present day atomic weights for silver, chlorine and bromine,<sup>12</sup> the results of Thorpe are here briefly summarized:

(1)	4Ag: TiCl <sub>4</sub> , whence atomic weight of titanium	= 48.02
(2)	4AgCl: TiCl <sub>4</sub> , " " " " "	= 48.13
(3)	TiCl <sub>4</sub> : TiO <sub>2</sub> , " " " " "	= 48.10
(4)	4Ag: TiBr <sub>4</sub> , " " " " "	= 48.11
(5)	4AgBr: TiBr <sub>4</sub> , " " " " "	= 48.12
(6)	TiBr <sub>4</sub> : TiO <sub>2</sub> , " " " " "	= 48.07

Mean..... 48.09

This value may be rounded off to Ti = 48.1.

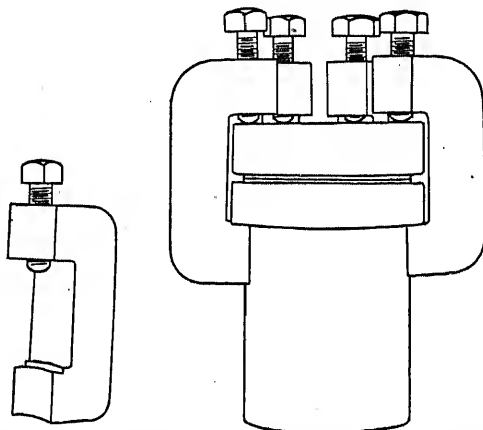
Rather recently, G. P. Baxter and G. J. Fertig<sup>13</sup> published a preliminary paper on the revision of the atomic weight of titanium, wherein the ratio of titanic chloride to silver was determined. Elaborate precautions were taken in the purification of the chloride, and the analyses were performed with all modern refinements. The results are lower than those of Thorpe, the average of the four most concordant values being 47.88 or, rounding off, 47.9.

### (3) THE PREPARATION AND PROPERTIES OF THE METAL.

On account of its high melting point, its great tendency to combine with oxygen, nitrogen and carbon at high temperatures and the readiness with which it forms alloys with the common metals, the preparation of metallic titanium in a state of purity has been fraught with considerable difficulty. Most of the early attempts led to the obtainment of a rather impure product. The nitrides particularly, because of their metallic appearance, were assumed to be the metal itself. Thus W. H. Wollaston<sup>14</sup> mistook the small copper-colored cubes of titanium cyanonitride, which are frequently found in the slag and metal from blast furnaces and in forge scale, for the metal, and it was not until much later that F. Wöhler<sup>15</sup> pointed out the true nature of this substance. J. J. Berzelius<sup>16</sup> is usually credited with being the first to isolate the element titanium, which he obtained as a black powder with a metallic streak by reducing potassium fluotitanate with potassium; but since this material was insoluble in hydrofluoric acid it could not have been titanium.<sup>17</sup> Rose,<sup>18</sup> Wöhler<sup>19</sup> and Wöhler and Deville<sup>20</sup> in attempting to produce the metal obtained only the nitrides. L. F. Nilson and Agai,tersson,<sup>21</sup> however, by reducing the tetrachloride with sodium in polyvalent steel cylinder, obtained a product containing about 95 per trivalent titanium, the principal impurity being the monoxide. Then manganese a operating at very high temperatures in his electric furnace, sembling theore or less carburetted metal by reduction of the dioxide

with carbon. His best results, however, were realized by melting together the carbide and oxide, using a current of 2,000 amperes and 60 volts. This gave a metal containing less than 5 per cent of carbon. On re-melting the regulus with titanous oxide, a product containing only 2 per cent of carbon was obtained, which was free from nitrogen and silicon. This was probably the closest approach to pure titanium that had been obtained by any one prior to the work of M. A. Hunter.<sup>28</sup>

Hunter followed three different lines of experimentation: the reduction of fluotitanates by alkali metals, the reduction of titanium dioxide by carbon and the reduction of titanium tetrachloride by sodium—the



(Rensselaer Polytechnic Institute, Engineering and Science Series, No. 1, p. 6, 1911.)

FIG. 9.—M. A. Hunter's bomb for preparing metallic titanium.

last being a modification of Nilson and Pettersson's process. The first two methods gave rather impure products, the first being contaminated with oxides and the second with carbide; but the third was successful and gave practically pure titanium.

By way of apparatus, Hunter employed a 1000 c.c. bomb (Figure 9) constructed of machine steel and capable of withstanding a total internal pressure of 80,000 pounds. The lid was firmly held down by six braces, there being an intervening gasket of soft copper.

On heating the bomb to low redness, the reaction takes place with explosive violence and is of only a moment's duration. The product obtained after cooling and washing consists for the most part of a thoroughly melted metal, but there are also present some 100°C. semi-molten powder and a little fine powder. The yield is 90 per cent of the theoretical—the loss being attributable to the fact that a some-



spite of precautions taken to prevent it. It is thus easy to prepare as much as 100 grams of virtually pure titanium in one experiment.

L. Weiss and H. Kaiser<sup>24</sup> obtained a somewhat impure metal (97.5 per cent) by reduction of the fluotitanate, the amorphous material being melted in a vacuum arc furnace.

Finally, M. Billy<sup>25</sup> has obtained titanium, perfectly free from iron,<sup>26</sup> by reducing titanium tetrachloride vapor with sodium hydride in a special apparatus constructed of glass. This metal contains hydrogen, from which it may be freed by heating to about 800°C. in vacuo.

There is much lack of agreement among statements in the literature regarding the properties of titanium; since many of the observations were made on very impure specimens of the metal and are therefore of little or no value. Hunter's<sup>27</sup> record, since his material was so nearly pure, may be considered reliable; provided it be borne in mind that in some instances he did not attempt to obtain quantitative data of high precision. A few other observations along with the respective authorities are included in the following account.

Titanium resembles polished steel in appearance. It is hard and brittle in the cold; but becomes malleable at a low red heat, and may be forged in much the same manner as wrought iron. Attempts to draw it into wire have not been successful. The specific heat rises rapidly with increase in temperature, the mean value being 0.1462 (0° to 100°C.) and 0.1563 (0° to 333°C.). The melting point given by the Bureau of Standards<sup>28</sup> is 1800°C., this value having been obtained by means of the micropyrometer on a sample prepared by H. v. Wartenberg. Metal made by the Titanium Alloy Manufacturing Company of Niagara Falls, presumably by Hunter's process, melted at the slightly lower temperature 1787°C. when tested with the same instrument.<sup>29</sup> The chief lines in the arc spectrum are 4999.6, 5014.3, 5193.1, 5210.5, (4008-5805) (13) and in the spark spectrum 3685.3, 3900.8, 4395.2, 4572.2 (2397-5648) (18).<sup>30</sup> The electrical resistivity is 3.19 microhms per cm. cube (Shukow).<sup>31</sup> The specific gravity of Hunter's material, whether forged or unforger, was found by him to be about 4.50. The carbon-free titanium of Hunter is much softer than that of Moissan,<sup>32</sup> which is described as being hard enough to scratch rock crystal. It will however make a distinct mark on window glass.

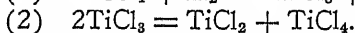
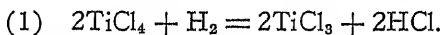
According to Moissan<sup>33</sup> titanium combines with oxygen with incandescence at 610°C., and, in the form of powder, burns in nitrogen at 800°C. At lower temperatures it is fairly stable in air, being attacked only slightly within the range 100°-200°C.<sup>34</sup> Hunter<sup>35</sup> records an trivalentment wherein a rod of metal 12 cm. long and 1.8 mm. in diameter manganen air at a temperature of 1200°C. when a current of 50 sembling the sent through it. The heat of oxidation was enough to

melt the oxide formed. All the halogen elements unite with titanium, at appropriate temperatures, giving the quadrivalent salts. When sufficiently hot, titanium combines with sulfur, phosphorus, carbon, boron and silicon. The powdered metal decomposes steam between 700°C. and 800°C.<sup>36</sup> Amorphous titanium absorbs hydrogen under certain conditions.<sup>37</sup> Moderately concentrated hydrochloric acid dissolves titanium slowly on boiling. Molten acid potassium sulfate and hot concentrated sulfuric acid are also capable of effecting solution. Hot nitric acid attacks it with formation of titanous acid. Hydrofluoric acid dissolves titanium very readily; but not without loss, owing to the volatility of titanium fluoride.

#### (4) TYPICAL COMPOUNDS.

##### Chlorides.

*Dichloride.* On account of its great instability under ordinary conditions, most if not all of the methods thus far proposed for the preparation of titanium dichloride have yielded a rather impure product, that is, containing either the metal or the trichloride. A. Stähler and F. Bachran,<sup>38</sup> utilizing the reaction first brought out by C. Friedel and J. Guérin,<sup>39</sup> pass a mixture of hydrogen and titanium tetrachloride through a cold-hot tube at 1100°C. and then heat the sublimate to 700°C. The reactions are as follows:



O. Ruff and F. Neumann<sup>40</sup> have studied the formation of titanium dichloride with special reference to the most favorable temperature and pressure. Still more recently G. S. Forbes and L. P. Hall<sup>41</sup> were able to obtain considerable quantities of the dichloride in admixture with the trichloride by treating finely divided metallic titanium with dry hydrogen chloride, the maximum temperature being between 350°C. and 400°C. The dichloride of titanium is described by Goerges and Stähler<sup>42</sup> as being a black powder. This statement is not incompatible with that of Forbes and Hall<sup>43</sup> to the effect that their mixture of chlorides was purplish-black in color. Furthermore, these investigators<sup>43</sup> found that the product turned purple in air, and when thus exposed would catch fire if slightly warmed. It could, however, be quickly dissolved in freshly boiled and partially frozen water in a vessel filled with carbon dioxide without noticeable decomposition; and, after filtration in a closed system, the solution could be kept at 0°C. in the absence of air without showing any appreciable change in the ratio of divalent to trivalent titanium. Titanium dichloride is a some-

what weaker reducing agent than chromous chloride, but it is immensely more sensitive to catalytic decomposition. Observation of the rapid rate at which hydrogen is evolved by titanium dichloride in aqueous solution in contact with certain substances has caused previous experimenters<sup>44</sup> to exaggerate its reducing power. Even when other conditions have been complied with, the acid concentration of the solution greatly affects the stability of this compound—0.10 N hydrochloric acid being the uppermost limit consistent with permanency.

*Trichloride (Titanous Chloride).* Of the many methods that have been used for the production of titanous chloride only two need be considered here as being of practical importance. The others may be dismissed for one or more of the following reasons: the process is inconvenient, the yield is small or the product is impure. On passing a mixture of hydrogen and titanous chloride vapor through a red hot tube violet scales of anhydrous titanous chloride condense partly on the cooler portion of the tube and partly in the receiver.<sup>45</sup> A more satisfactory method depends on reducing a solution of titanous chloride, containing more or less hydrochloric acid, by means of the electric current. From such a solution violet crystals of the hexahydrate may be obtained by vacuum concentration.<sup>46</sup> The anhydrous crystals have a brilliant luster, do not fume in air, are not volatile at ordinary temperatures, but decompose readily on being heated. The needle-like crystals of the hydrated salt deliquesce and emit fumes on exposure to air. The trichloride of titanium is freely soluble in water and in alcohol but insoluble in ether. The dilute aqueous solution changes in color from wine-red to violet as the acidity increases. The alcoholic solution is green. It combines rather rapidly with oxygen in the presence of water to form the titanous salt; hence solutions should not be kept in the open air.

*Tetrachloride (Titanic Chloride).* Since titanium dioxide does not react with hydrochloric acid to any great extent, it has been found necessary to reduce the oxide by some suitable means in order to bring about combination between titanium and chlorine. Many years ago, J. B. A. Dumas,<sup>47</sup> prepared titanium tetrachloride by subjecting a mixture of titanous oxide and carbon maintained at red heat to the action of chlorine. Others<sup>48</sup> have used this process more or less successfully, and Thorpe<sup>49</sup> was able to obtain titanous chloride in considerable quantity by it, using a mixture of precipitated titanous oxide and lampblack, which needed but little purification. The chlorination of titanium carbide,<sup>50</sup> of ferro-titanium<sup>51</sup> and the reduction of titanous oxide by aluminum<sup>52</sup> according to the Goldschmidt process<sup>53</sup> prior to chlorination have all been employed by various investigators—the first and last having given apparently good results. The treatment of titanous oxide with a volatile

substance of both reducing and chlorinating nature, such as sulfur monochloride, chloroform or carbon tetrachloride, or with a mixture of carbon monoxide and chlorine would seem to be of doubtful propriety.<sup>54</sup> L. E. Barton,<sup>55</sup> in describing a patented process, has laid stress on the desirability of having the material to be chlorinated neither in large compact pieces nor in fine powder but rather in porous lumps of fair size. To this end he mixes the oxide (natural or artificial) with soft coal of good coking quality and ignites without access of air. The reaction takes place in the residual mass at a somewhat lower temperature than has heretofore been thought necessary, 650°C. being quite satisfactory. It is thus possible by controlling the heat to distil over most of the titanium before the iron chloride begins to form. In other words, the first fraction consists of nearly pure titanic chloride. The crude distillate may be purified according to Hunter<sup>56</sup> by refluxing in a current of nitrogen to remove chlorine and then repeatedly distilling, the end fractions being rejected. The portion boiling between 136°C. and 137°C. is shaken with mercury and sodium amalgam. On redistillation a water-white titanic chloride of constant boiling point should be obtained. Titanium tetrachloride is a transparent, colorless, mobile, strongly refracting liquid, having a density of 1.7604 at 0°C. and boiling at 136.4°C. at 760 mm.<sup>57</sup> Its melting point is -23°C.<sup>58</sup> It fumes vigorously in moist air, being actively hydrolyzed to titanic acid (or intermediate basic chlorides) and hydrochloric acid with evolution of much heat. The precipitate formed on adding titanic chloride to cold water dissolves in time, if the solution be not too dilute, and especially if acid be present. When poured into concentrated hydrochloric acid, it dissolves giving a clear yellow solution, which probably contains the acid  $\text{H}_2\text{TiCl}_6$ ; since salts of this type are known<sup>59</sup> (Table II.). Titanic chloride also exhibits the peculiar property of forming stable additive compounds with certain organic as well as with certain inorganic substances (Table II.).

### Fluorides.

Only two fluorides of titanium are known: the violet trifluoride and the colorless tetrafluoride. Although fluotitanic acid is known only in solution, fluotitanates of more than a dozen different metals have been described. Of these the sodium, potassium and barium salts are of interest in that they have all been experimented with in attempts to prepare the metal (p. 42). Potassium fluotitanate, which is by far the most important of all the metallic fluotitanates, is easily made by dissolving titanic oxide in hydrofluoric acid and nearly neutralizing the diluted solution with potassium hydroxide; whereupon the hydrated salt,  $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ , separates out on cooling. It may be purified by

crystallization from hot water containing a little hydrofluoric acid to prevent the formation of a basic compound. Potassium fluotitanate crystallizes in white leaflets. On being heated to  $150^{\circ}\text{C}$ . it is completely converted into the anhydrous salt,  $\text{K}_2\text{TiF}_6$ . It is only sparingly soluble in cold water: 100 cc. of water at  $0^{\circ}\text{C}$ . dissolves 0.556 gram of  $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ <sup>60</sup>; but it becomes much more soluble as the temperature approaches  $100^{\circ}\text{C}$ .

### Bromides.

Titanium forms tri- and tetra-bromides. The hydrated tribromide,  $\text{TiBr}_3 \cdot 6\text{H}_2\text{O}$ , may be prepared by electrolytic reduction of the tetrabromide. It is violet in color and less stable than the corresponding chloride.<sup>61</sup> Thorpe<sup>62</sup> has prepared titanium tetrabromide by acting on the tetrachloride with dry hydrogen bromide. He gives the following account of its properties: "It is a beautifully crystalline substance of a dark-yellow or orange color, melting at about  $40^{\circ}\text{C}$ ., and boiling at  $229^{\circ}\text{C}$ . (uncorrected). It is very hygroscopic, and is readily decomposed by water with the evolution of comparatively little heat and with the production of a perfectly clear solution".

### Iodides.

The di-iodide is black,<sup>63</sup> the tri-iodide,  $\text{TiI}_3 \cdot 6\text{H}_2\text{O}$ , is violet and more instable than the corresponding bromide<sup>64</sup> and the tetra-iodide is reddish brown with golden reflections and metallic luster.<sup>65</sup>

### Oxides.

*Monoxide.* There may be some doubt as to whether this oxide has yet been prepared in a state of purity. It may be obtained, however, contaminated with other substances, chiefly titanium carbide, by subjecting a mixture of titanium dioxide and carbon to a rather high temperature with exclusion of air.<sup>66</sup> Moreover, Billy<sup>67</sup> claims to have gotten the monoxide by reducing the dioxide with metallic titanium at  $1400^{\circ}$ - $1500^{\circ}\text{C}$ .

*Sesquioxide (Titanous Oxide).* J. J. Ebelmen<sup>68</sup> has prepared the sesquioxide of titanium by reducing the dioxide with hydrogen at a high temperature. Friedel and Guérin<sup>69</sup> have obtained a seemingly better crystallized product by heating the dioxide to whiteness in a current of hydrogen and titanium tetrachloride vapor. Finally, Billy<sup>67</sup> has reduced the dioxide with titanium between  $900^{\circ}\text{C}$ . and  $1000^{\circ}\text{C}$ . and under otherwise suitable conditions. It forms black lustrous crystals, isomorphous with hematite. It is insoluble in hydrochloric acid and in nitric acid; but it is soluble in sulfuric acid.

*Dioxide (Titanic Oxide).* The three minerals, rutile, brookite and anatase, which are composed essentially of titanium dioxide, have already been treated in Chapter II. It is interesting to note that all three of these physically different forms of titanic oxide may be reproduced by artificial means.<sup>70</sup> The amorphous compound,  $\text{TiO}_2$ , may be prepared by igniting the hydroxide (titanic acid)—the latter being obtained by hydrolysis of a titanic salt, either by adding ammonium hydroxide in excess or by boiling the nearly neutral and rather dilute solution. Starting with rutile or ilmenite, pure titanic oxide may be prepared in a variety of ways. Some of these methods are practicable only when small quantities are to be made in the laboratory, while others (patented processes) are adapted to large scale commercial production. Only a few examples will be given here. Any satisfactory method for preparing titanic chloride furnishes an excellent starting point; since this compound may be dissolved in water and titanic acid precipitated from such a solution. Finely powdered rutile may be fused with about six times its weight of potassium pyrosulfate and the melt extracted with cold water. On adding ammonium sulfide the iron will be precipitated as sulfide and the titanium as hydroxide. If this precipitate, after having been filtered and washed, is suspended in water and the solution gassed with sulfur dioxide, the iron dissolves and the titanium remains behind. This procedure may be altered by precipitating the iron as sulfide in the presence of ammonium tartrate, acidifying the iron-free filtrate with sulfuric acid, evaporating until the tartaric acid begins to char and froth and then completing the oxidation of the organic matter by the careful addition of fuming nitric acid.<sup>71</sup> Amorphous titanium dioxide is a white powder, which transiently acquires a lemon-yellow tint on being heated. Its specific gravity varies according to the temperature to which it has been subjected, being 3.89-3.95 for 600°C., 4.13 for 800°C. and 4.25 for 1000°-1200°C.<sup>72</sup> It has a high refractive index: 2.2 for the amorphous material, 2.52 for anatase, 2.64 for brookite and 2.71 for rutile (toward air with sodium light).<sup>73</sup> On being heated to 950°C. it becomes cryptocrystalline and consequently undergoes an increase in refractive index as compared with the uncrystallized substance.<sup>73</sup> Its specific heat between 0°C. and 100°C. is 0.1785, which however increases with rise in temperature,<sup>74</sup> and it melts at 1560°C.<sup>75</sup> The heat of formation of the dioxide, as determined by W. G. Mixer,<sup>76</sup> is 215,600 cal. on oxidizing the metal by sodium peroxide to amorphous titanic oxide and 218,400 cal. by combustion of the finely divided metal in oxygen to the crystalline form. Titanic oxide is insoluble in water and practically insoluble in the ordinary dilute acids. Concentrated hydrochloric acid, concentrated nitric acid and aqua regia do not act on it to any great extent. It is readily

soluble in hydrofluoric acid on warming, and hot concentrated sulphuric acid slowly converts it into titanous sulfate, which in turn is soluble in water, if sufficient acid be present. The addition of an alkali sulfate to the sulfuric acid greatly hastens solution. Fusion with potassium pyrosulfate yields a melt which dissolves readily in cold dilute sulfuric acid (5 per cent by volume) or even in cold water.

### Hydroxides.

*Trihydroxide (Titanous Hydroxide).* On adding ammonium hydroxide to a solution of a titanous salt a black precipitate of titanous hydroxide is formed; but the substance is very instable. Even at ordinary temperatures it decomposes water with liberation of hydrogen, and is itself oxidized to white titanous hydroxide.

*Tetrahydroxide (Titanic Hydroxide, or Titanic Acid).* The properties of titanous acid vary according to the conditions under which it is formed. On the one hand, when precipitated by ammonium hydroxide from a cold solution of a titanium salt, it forms a voluminous white precipitate, which is readily soluble in dilute acid; though even this is said to pass partially into the insoluble form if kept in contact with water for a sufficient length of time.<sup>77</sup> On the other hand, prolonged boiling of a slightly acid solution of titanous sulfate produces a very finely divided precipitate, which is practically insoluble in dilute acids, and which is inclined to form an opalescent colloidal suspension in water. T. Graham<sup>78</sup> has obtained colloidal titanous acid by dialysis. On being heated titanous acid suffers gradual loss of water and is completely dehydrated at approximately 710°C., as T. Carnelley and J. Walker<sup>79</sup> have shown.

### Titanates.

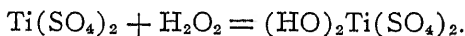
Anhydrous alkali titanates may be prepared by fusing the dioxide with alkali carbonate or hydroxide. The sodium and potassium salts,  $\text{Na}_2\text{TiO}_3$  and  $\text{K}_2\text{TiO}_3$ , thus obtained are said to form acid titanates on being leached with water. The latter are nearly though not quite insoluble in water, the potassium compound being slightly more soluble than the sodium compound, but are completely soluble in strong hydrochloric acid. In addition to these, titanates of many other metals have been prepared artificially, some of which are chemically identical with those that occur in nature.<sup>80</sup>

### Titanium Peroxide and Per-Salts.

Peroxide of titanium may be prepared, according to A. Classen,<sup>81</sup> by adding titanium tetrachloride drop by drop with stirring to dilute

alcohol, then hydrogen peroxide in large excess and finally ammonium hydroxide, ammonium carbonate or potassium hydroxide; whereupon a yellow precipitate forms after a short time. When dried on a tile, its composition is approximately represented by the formula  $\text{Ti}(\text{OH})_6$ , or  $\text{TiO}_3 \cdot 3\text{H}_2\text{O}$ . It is apt to be impure due to obstinate retention of water and salts. It is a yellow substance with active oxidizing properties.

The orange color that develops on adding hydrogen peroxide to a solution of a titanic salt has generally been supposed to be due to the formation of a salt of sexivalent titanium. There is considerable room for doubt, however, as to just what the orange colored compound really is. As the outcome of his studies on the subject, P. Faber,<sup>82</sup> was led to the conclusion that titanium is sexivalent in such compounds and that the two hydroxyl groups of hydrogen peroxide are directly united to the titanium atom. Thus:



Another view of at least some plausibility would be that titanium does not have a valence higher than four, and that in per-compounds two oxygen atoms are joined to each other as in hydrogen peroxide and these in turn to the titanium atom ( $\text{O}_2\text{TiSO}_4$ ). In recent work on titanium, Billy<sup>88</sup> has produced evidence favoring a pentavalent condition for the titanium in per-salts. This question, however, is of no immediate concern to the analyst; since peroxidized solutions of titanium are used only for color comparison, for purposes of separation or as a means of ascertaining the end-point in certain titrations, no stoichiometrical relationship depends upon the valence of titanium; consequently it need be given no further exposition in a work of this kind.

### Sulfates.

*Trisulfate (Titanous Sulfate).* Titanous sulfate is best obtained in solution by electrolytic reduction of titanic sulfate. The solution may not contain too great a quantity of free sulfuric acid. Factors affecting the electrolysis, such as cathode material, current density, temperature and so on, have been carefully studied by B. Diethelm and F. Foerster.<sup>84</sup> It is a very strong reducing agent, being more susceptible to atmospheric oxidation than titanous chloride;<sup>85</sup> hence it is not customary to attempt its isolation in solid form. H. Spence,<sup>86</sup> in accordance with a patented process, produces a double sulfate of titanium and sodium,  $\text{Ti}_2\text{Na}_2(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$ , in crystallized condition, which is stable in air if kept dry. It is also a matter of interest that titanous sulfate forms alums with rubidium and caesium sulfates.<sup>87</sup>



*Tetrasulfate (Titanic Sulfate).* Because of the ease with which it is hydrolyzed the isolation of the normal sulfate of quadrivalent titanium presents some difficulty. Neutral sulfates are, however, mentioned in the literature.<sup>88</sup> But it is of special interest to note that the Titanium Pigment Company, Inc., is now producing commercially a sulfate that corresponds to the formula  $\text{Ti}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ . This compound is described as being a substantially white substance, which, when examined microscopically under low magnification, appears to be thoroughly crystalline.<sup>89</sup> On the other hand, salts of varying degrees of basicity are well known. Processes for the preparation of basic sulfates have been patented<sup>90</sup>—likewise a double basic compound of titanium sulfate and sodium sulfate.<sup>91</sup> These sulfates are sometimes used as intermediate products for the manufacture of other titanium compounds that are directly applicable in the arts.

### Phosphates.

The precipitate produced by adding a soluble phosphate to a solution of titanic salt is more or less basic and of indefinite composition.<sup>92</sup> More definite phosphates may be obtained by fusing titanic oxide with phosphoric acid or an alkali phosphate.<sup>93</sup>

### Organic Compounds.

*Oxalates.* Several oxalates containing titanium have been prepared and described, but most of these are unimportant. One, however, has a good deal of practical value, viz., titanium potassium oxalate,  $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ . If a solution of potassium acid oxalate is saturated with titanic acid, titanium potassium oxalate may be crystallized out in the form of white needles. This salt is soluble in water without decomposition and is not appreciably hydrolyzed even when the solution is boiled.<sup>94</sup>

*Other Organic Derivatives.* Titanium has been substituted in or added to a considerable number and variety of organic substances. Only a few that have been claimed to possess useful properties will be mentioned here. These are: titanous thiocyanate,<sup>95</sup> titanic lactate,<sup>96</sup> titanic glycolate,<sup>97</sup> titanic tartrate,<sup>98</sup> etc. . . .

### Carbide.

P. W. Shimer<sup>99</sup> is credited with having discovered titanium carbide. He observed crystals in the residue left on dissolving pig iron in hydrochloric acid, which on analysis turned out to have the formula  $\text{TiC}$ . Moissan<sup>100</sup> obtained the carbide synthetically by heating a mixture of

titanic oxide and carbon in the electric furnace. Titanium carbide is not attacked by hydrochloric acid nor does it decompose steam at  $700^{\circ}\text{C}.$ , but with these exceptions it resembles titanium in chemical behavior.

### Cyanonitride (Carbonitride).

This substance was first prepared by Wöhler<sup>101</sup> by fusing together titanic oxide and potassium ferrocyanide. It is formed when nitrogen or air is passed over a mixture of titanium dioxide and carbon maintained at a fairly high temperature (about  $1450^{\circ}\text{C}.$ ). The formula  $\text{Ti}_2\text{CN}_4$  is usually assigned to this material, but it is probably not a definite compound; since T. W. Hogg<sup>102</sup> found that the specific gravity of different specimens varied from 4.1 to 5.1 and the titanium content from 60.5 to 79.8 per cent. It crystallizes in reddish cubes and sometimes displays a beautiful iridescent surface. It is very hard and resistant to the action of acids. When heated in steam it yields ammonia.

### Nitrides.

*Trinitride (Titanous Nitride).* Owing to the special affinity of titanium for nitrogen the nitride is formed in all reductions in which air is not excluded, provided the temperature be not too high. Titanous nitride may be prepared in a variety of ways, notably by the method of Friedel and Guérin,<sup>103</sup> which consists in allowing gaseous ammonia to act on titanic oxide at a suitable temperature. This nitride is described as being a massive substance resembling bronze in appearance, hard enough to scratch topaz and of density 5.18 at  $18^{\circ}\text{C}.$  It is acted on by potassium hydroxide with disengagement of ammonia.<sup>104</sup>

*Tetranitride (Titanic Nitride).* Titanic nitride,  $\text{Ti}_3\text{N}_4$ , is supposed to be formed when titanium tetrachloride and ammonium chloride vapors are passed into a red hot tube previously filled with hydrochloric acid gas,<sup>105</sup> or when the double compound,  $\text{TiCl}_4 \cdot 4\text{NH}_3$ , is heated alone.<sup>106</sup> It is said to be a copper-red substance with metallic luster.<sup>107</sup> Ruff and Eisner,<sup>108</sup> however, have cast some doubt on the existence of this compound.

### Sulfides.

Sulfides corresponding to three valences of titanium are known, viz., monosulfide, sesquisulfide and disulfide. The first two are prepared by reduction of the disulfide.

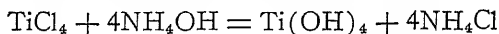
Titanic sulfide is obtained in a state of approximate purity when a mixture of titanic chloride vapor and hydrogen sulfide is led through a heated tube. It forms brass-yellow crystals that look like mosaic gold. It is on the whole a rather stable substance when pure, being insoluble

in water, hydrochloric acid and sulfuric acid. On the other hand, it is attacked by chlorine, dissolved by aqua regia and decomposed at a bright red heat by steam.<sup>109</sup>

### (5) REACTIONS OF ANALYTICAL VALUE.

#### Precipitation Tests.<sup>110</sup>

1. *Ammonium hydroxide* precipitates, at ordinary temperatures, white gelatinous titanic acid, which is insoluble in an excess of the reagent, but readily soluble in dilute mineral acids.



The same reaction when carried out at the boiling temperature gives rise to a form of titanic acid that is difficultly soluble in acids (p. 50).

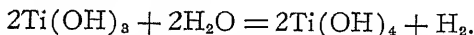
Potassium or sodium hydroxide may be substituted for the ammonia solution; but the precipitate is slightly soluble in an excess of the precipitant.<sup>111</sup>

Ammonium sulfide and barium carbonate (from a solution of titanic chloride) in the cold, and several weakly basic hydrolytic agents at or near the boiling temperature precipitate titanium completely. Among the latter are alkali acetates, sodium thiosulfate, phenylhydrazine, aniline, etc.

Titanium is also quantitatively thrown down by prolonged boiling of a largely diluted solution of the sulfate containing only a small quantity of sulfuric acid in the form of a finely divided precipitate. A nearly neutral solution of the chloride (free from sulfates) is much more quickly hydrolyzed on boiling and gives a precipitate that is more easily filtered and washed.

Many organic substances, particularly citric and tartaric acids, and pyrophosphates either seriously interfere with or altogether prevent the above reactions. Potassium cyanide, however, does not exert any disturbing influence on the precipitating action of ammonium hydroxide.<sup>112</sup>

On cautiously adding an alkali hydroxide to a solution of a titanous salt the color becomes bluer; but as soon as the alkali is present in excess, the whole of the titanium is precipitated as black titanous hydroxide, which gradually turns white (more rapidly on warming) with evolution of hydrogen.



E. Knecht and E. Hibbert<sup>113</sup> have observed that, in the case of titanous chloride prepared by the action of tin and hydrochloric acid on titanic chloride, the black precipitate formed by adding sodium hydroxide in

TABLE II.  
 REPRESENTATIVE COMPOUNDS OF TITANIUM.

No.	Name	Formula	Authority
1	Acetate .....	$\text{NaTi}_2(\text{OH})_2(\text{C}_2\text{H}_3\text{O}_2)_6 \cdot 4\text{H}_2\text{O}$	Stähler <sup>1</sup>
2	Arsenite .....	$\text{Ti}_6\text{O}_8(\text{AsO}_2)_4$	Reichard <sup>2</sup>
3	Boride .....	Unestablished.	Wedekind <sup>3</sup>
4	Bromides and Related Compounds.	$\text{TiBr}_3 \cdot 6\text{H}_2\text{O}$ $\text{TiBr}_3$ $\text{Ti}(\text{OH})\text{Br}_3$ (?) $\text{TiBr}_3 \cdot 8\text{NH}_3$ (approx.) $\text{H}_2\text{TiBr}_6$ (in solution) $(\text{NH}_4)_2\text{TiBr}_6 \cdot 2\text{H}_2\text{O}$	Rosenheim and Schütte <sup>4</sup> Ruff and Treidel <sup>5</sup> Rosenheim and Schütte <sup>4</sup> " " "
5	Carbide .....	$\text{TiC}$	
6	Chlorides and Related Compounds.	$\text{TiCl}_2$ $\text{TiCl}_3$ , $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ $\text{TiCl}_4$ $\text{Ti}(\text{OH})\text{Cl}_3$ $\text{TiCl}_4 \cdot 8\text{NH}_3$ $\text{TiCl}_4 \cdot \text{PCl}_5$	Stähler <sup>1</sup> Tüttchew <sup>6</sup>
	<i>Pyridine Addition Compound</i> .....	$\text{TiCl}_4 \cdot 6\text{C}_5\text{H}_5\text{N}$ $\text{H}_2\text{TiCl}_6$ , or $\text{H}_4\text{TiCl}_8$ (in solution) $(\text{NH}_4)_2\text{TiCl}_6 \cdot 2\text{H}_2\text{O}$	Rosenheim and Schütte <sup>4</sup> " " " " " " " " "
	<i>Aniline Salt</i> .....	$4\text{C}_6\text{H}_5\text{NH}_2 \cdot \text{H}_4\text{TiCl}_8$	
7	Chromate .....	$\text{Ti}_2\text{O}_3\text{CrO}_4 \cdot 2\text{H}_2\text{O}$	Blondel <sup>8</sup>
8	Citrate .....	$\text{H}_2\text{K}_2\text{TiO}(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot \text{H}_2\text{O}$	Henderson, Orr and Whitehead <sup>7</sup>
9	Fluorides and Related Compounds.	$\text{TiF}_3$ $\text{TiF}_4$ $\text{TiF}_4 \cdot 2\text{NH}_3$ $\text{K}_2\text{TiF}_6$ $\text{H}_2\text{TiF}_6$ (in solution) $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ $2\text{BaTiF}_6 \cdot \text{H}_2\text{O}$ $\text{KCuTiF}_6 \cdot 4\text{H}_2\text{O}$	Weber <sup>9</sup> Ruff and Plato <sup>10</sup> Ruff and Ipsen <sup>11</sup> Piccini <sup>12</sup> Ruff and Ipsen <sup>11</sup>
	<i>Quinine Salt</i> .....	$\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$	Emich <sup>13</sup>
10	Formate .....	$\text{K}_2\text{Ti}_4(\text{OH})_8(\text{CHO}_2)_{11}$	Schaeffer <sup>14</sup>
11	Hydride .....	$\text{Ti}_3\text{H}_8$	Stähler and Bachran <sup>15</sup>
12	Hydroxides .....	$\text{Ti}(\text{OH})_3$ $\text{Ti}(\text{OH})_4$ $\text{Ti}(\text{OH})_4$ , or $\text{TiO}(\text{OH})_2$ $\text{Ti}(\text{OH})_6$ , or $\text{TiO}_2 \cdot 3\text{H}_2\text{O}$	Billy <sup>16</sup> Goerges and Stähler <sup>17</sup> Knecht <sup>18</sup>
13	Iodides and Related Compounds .....	$\text{TiI}_2$ $\text{TiI}_3 \cdot 6\text{H}_2\text{O}$ $\text{TiI}_4$ $\text{H}_2\text{TiI}_6$ (in solution)	Rosenheim and Schütte <sup>4</sup>
14	Nitrate .....	$\text{Ti}_6\text{O}_8(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Merz <sup>19</sup>
15	Nitrides and Related Compounds	$\text{TiN}$ $\text{Ti}_3\text{N}_4$	
	<i>Cyanonitride</i> .....	$\text{Ti}_3\text{CN}_4$ (?)	

TABLE II. (Cont.)

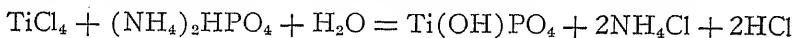
No.	Name	Formula	Authority
16	Oxalates .....	$\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ $\text{Ti}_3\text{O}_5\text{C}_2\text{O}_4 \cdot 12\text{H}_2\text{O}$ $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	Stähler <sup>1</sup> Rosenheim and Schütte <sup>2</sup> " " "
17	Oxides .....	$\text{TiO}$ $\text{Ti}_2\text{O}_3$ $\text{TiO}_2$ $\text{TiO}_3$ (?)	
18	Per-Compounds ...	$\text{Na}_2\text{O}_2 \cdot \text{TiO}_2 \cdot 3\text{H}_2\text{O}$ $(\text{NH}_4)_3\text{TiO}_2\text{F}_5$ $\text{K}_2\text{TiO}_2(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$	Melikoff and Pissarjewsky <sup>30</sup> Piccini <sup>12</sup> Mazzucchelli and Pantaneli <sup>21</sup>
19	Phosphates .....	$\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$ $\text{K}_2\text{Ti}_2\text{O}_2(\text{PO}_4)_2$ $\text{TiP}_2\text{O}_7$	Merz <sup>19</sup> Ouvrard <sup>22</sup> Hautefeuille and Margottet <sup>23</sup>
20	Phosphide .....	$\text{TiP}$ (?)	Gewecke <sup>24</sup>
21	Silicides .....	$\text{Ti}_2\text{Si}$ $\text{TiSi}_2$	Lévy <sup>25</sup> Hönigschmidt <sup>26</sup>
22	Sulfates .....	$\text{Ti}_2(\text{SO}_4)_3$ $\text{TiOSO}_4$ $\text{Ti}_2\text{O}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$ $\text{CsTi}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ $\text{Na}_2\text{Ti}_2(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$	Merz <sup>19</sup> Blondel <sup>27</sup> Piccini <sup>28</sup> Spence <sup>30</sup>
23	Sulfides .....	$\text{TiS}$ $\text{Ti}_2\text{S}_3$ $\text{TiS}_2$	
24	Tartrate .....	$\text{Na}_2\text{TiO}(\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 8\text{H}_2\text{O}$	Henderson, Orr and Whitehead <sup>7</sup>
25	Thiocyanates .....	$\text{K}_2\text{Ti}(\text{CNS})_6 \cdot 6\text{H}_2\text{O}$ $\text{TiO}(\text{CNS})_2 \cdot 2\text{H}_2\text{O}$	Stähler <sup>1</sup> Rosenheim and Cohn <sup>30</sup>
26	Titanates .....	$\text{Mg}_2\text{TiO}_4$ $(\text{C}_6\text{H}_5)_4\text{TiO}_4$ $\text{MgTiO}_3$ $\text{Na}_2\text{Ti}_2\text{O}_5$ $\text{Zn}_2\text{Ti}_2\text{O}_7$ $\text{CaTiSiO}_5$	Hautefeuille <sup>31</sup> Bischoff and Adkins <sup>32</sup> Hautefeuille <sup>31</sup> Cormimboeuf <sup>33</sup> Lévy <sup>34</sup> Hautefeuille <sup>31</sup>
27	Titanosilicate .....		
28	Other Organic Com- pounds		
	<i>Lactates</i> .....	$\text{HTiO}_2\text{M}_3(\text{C}_3\text{H}_5\text{O}_3)_4$ (?)	Dreher <sup>35</sup>
	<i>Thymate</i> .....	$\text{Ti}(\text{OC}_{10}\text{H}_{17})_4$	Lévy <sup>34</sup>
	<i>Salicylate</i> .....	$\text{H}_2\text{Ti}(\text{C}_6\text{H}_4\text{O}_3)_3$	Rosenheim and Sorge <sup>36</sup>
	<i>Dihydroxymaleate</i> Derivative of <i>Nitrosophenyl-</i> <i>hydroxylamine</i>	$2(\text{TiO}_2\text{H})_2\text{C}_4\text{H}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$ $\text{Ti}(\text{C}_6\text{H}_4\text{N}_2\text{O}_2)_4$	Fenton <sup>37</sup> Bellucci and Grassi <sup>38</sup>

<sup>1</sup> Stähler: Ber., 38, 2619 (1905).<sup>2</sup> Reichard: ibid., 27, 1019 (1894).<sup>3</sup> Wedekind: ibid., 46, 1198 (1913).<sup>4</sup> Rosenheim and Schütte: Z. anorg. Chem., 26, 239 (1901).<sup>5</sup> Ruff and Treidel: Ber., 45, 1364 (1912).<sup>6</sup> Tütttschew: Ann., 141, 111 (1867).<sup>7</sup> Henderson, Orr and Whitehead: J. Chem. Soc., 75, 542 (1899).<sup>8</sup> Blondel: Bull. soc. chim., (3) 19, 218 (1898).

excess is remarkably stable and decomposes much more slowly than specimens of titanous hydroxide that have been obtained by other methods.

On adding ammonium hydroxide to a solution of titanium containing a considerable quantity of hydrogen peroxide the orange color of the solution is bleached to pale yellow; but there is no precipitation at once. On long standing, however, a yellow deposit makes its appearance, which is probably pertitanic hydroxide.

2. *Ammonium phosphate* produces, even in rather strongly acidulated solutions, a white and difficultly filterable precipitate of more or less basic titanic phosphate of somewhat indefinite composition.



Even in the presence of tartaric acid titanium is completely thrown out as phosphate when the solution is boiled;<sup>114</sup> while in cold solutions containing a sufficient quantity of hydrogen peroxide no precipitate forms (difference from zirconium).<sup>115</sup>

3. *Potassium ferrocyanide* gives a finely divided brown precipitate. A small amount of iron causes the color to be green, because of an admixture of Prussian blue.

<sup>9</sup> Weber: J. prakt. Chem., 90, 212 (1863).

<sup>10</sup> Ruff and Plato: Ber., 37, 673 (1904).

<sup>11</sup> Ruff and Ipsen: *ibid.*, 36, 1777 (1903).

<sup>12</sup> Piccini: Compt. rend., 97, 1064 (1883).

<sup>13</sup> Emich: Monats., 25, 907 (1904).

<sup>14</sup> Schaeffer: J. Am. Chem. Soc., 30, 1862 (1908).

<sup>15</sup> Stähler and Bachran: Ber., 44, 2906 (1911).

<sup>16</sup> Billy: Ann. chim., 16, 5 (1921).

<sup>17</sup> Goerges and Stähler: Ber., 42, 3200 (1909).

<sup>18</sup> Knecht: *ibid.*, 36, 166 (1903).

<sup>19</sup> Merz: J. prakt. Chem., 99, 157 (1866).

<sup>20</sup> Melikoff and Pissarjewsky: Ber., 31, 953 (1898).

<sup>21</sup> Mazzucchelli and Pantanelli: Gazz. chim. ital., 40, I, 666 (1910).

<sup>22</sup> Ouvrard: Compt. rend., 111, 177 (1890).

<sup>23</sup> Hautefeuille and Margottet: *ibid.*, 102, 1017 (1886).

<sup>24</sup> Gewecke: Ann., 361, 79 (1908).

<sup>25</sup> Lévy: Compt. rend., 121, 1148 (1895).

<sup>26</sup> Hönigschmidt: *ibid.*, 143, 224 (1906).

<sup>27</sup> Blondel: Bull. soc. chim., (3) 21, 262 (1899).

<sup>28</sup> Piccini: Z. anorg. Chem., 17, 355 (1898).

<sup>29</sup> Spence: U. S., 758,710, May 3, 1904.

<sup>30</sup> Rosenheim and Cohn: Z. anorg. Chem., 28, 167 (1901).

<sup>31</sup> Hautefeuille: Ann. chim. phys., (4) 4, 129 (1865).

<sup>32</sup> Bischoff and Adkins: J. Am. Chem. Soc., 46, 256 (1924).

<sup>33</sup> Cormimboeuf: Compt. rend., 115, 823 (1892).

<sup>34</sup> Lévy: Ann. chim. phys., (6) 25, 433 (1892).

<sup>35</sup> Dreher: U. S., 760,319, May 17, 1904.

<sup>36</sup> Rosenheim and Sorge: Ber., 53B, 932 (1920).

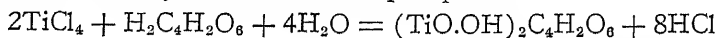
<sup>37</sup> Fenton: J. Chem. Soc., 93, 1064 (1908).

<sup>38</sup> Bellucci and Grassi: Gazz. chim. ital., 43, I, 570 (1913).

4. *Tannic acid* produces a brown precipitate, which soon turns orange-red, when added to slightly acidified and fairly concentrated solutions of titanium. With traces a yellow coloration is produced. The color is bleached out by acids; but it is largely, if not entirely, restored by alkalis. Citric acid delays but does not prevent the formation of the precipitate.

The test is a delicate one; but it may be entirely vitiated by iron, due to the overpowering effect of black ferric tannate. But the iron may be removed as sulfide by passing hydrogen sulfide into an ammoniacal solution containing also ammonium citrate. After acidifying and boiling the filtrate, and again filtering so as to eliminate coagulated sulfur, the tannic acid reaction will be in order.

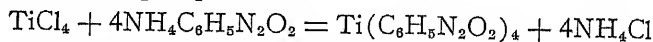
5. *Dihydroxymaleic acid* gives in warm and not too dilute solutions of titanium a bulky chocolate-colored precipitate.



From more dilute and cold solutions no precipitate is formed but an intense orange-red color instead, which appears to be of colloidal nature; since the colored substance is coagulated by boiling or even on long standing. The color varies somewhat with dilution, being orange-red at 1 : 15,000, lemon-yellow at 1 : 150,000 and straw-yellow at 1 : 1,000,000. By looking through a column 30 cm. long, it is easy to observe the color at a dilution of 1 : 5,000,000. In the opinion of its discoverer,<sup>116</sup> the dihydroxymaleic acid reaction is from 15 to 20 times as delicate as the hydrogen peroxide test.

Titanium may be thus identified in the presence of vanadium (vanadic acid), the latter yielding only a blue solution. Molybdenum (molybdates) and uranium (uranyl salts) give red or brown colors, but these are readily distinguished from titanium, since they are destroyed by acids, the former on heating and the latter at ordinary temperatures. Tungsten (tungstic acid) forms a brown color, which quickly changes to blue. Iron (ferric salts) interferes by oxidizing the reagent; but this difficulty may be overcome by adding the compound in large excess when only traces of iron are present or by prior reduction with sulfur dioxide when iron accompanies the titanium in greater quantity. Thorium, cerium, zirconium and tin give negative results. Fluorine in sufficient quantity prevents the reaction entirely.

6. The *ammonium salt of nitrosophenylhydroxylamine* ("*cupferon*") produces, even in highly acidified solutions of titanium, a flocculent canary-yellow precipitate.<sup>117</sup>



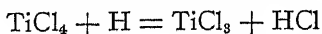
It is necessary to carry out the precipitation in the cold; since the compound appears to melt below the temperature of boiling water, forming

an oil of darker color, which solidifies on cooling to a resinous body. There is little or no tendency to form a colloidal suspension—a thoroughly coagulated precipitate forming almost immediately on adding the reagent to a very dilute solution of titanium. The reaction is independent of many kinds of organic matter,<sup>118</sup> including tartaric acid, citric acid and other hydroxyacids.

Iron (ferric salts) is completely thrown out by the cupferron reagent in the form of a brown precipitate; but its prior removal as sulfide involves no difficulty.<sup>119</sup> Copper yields a blue-gray precipitate, which is soluble in ammonium hydroxide. Zirconium, thorium and tin (stannic salts) give white precipitates; while vanadium (vanadic acid) and uranium (uranous salts) form red and brown insoluble compounds respectively. Likewise, columbium and tantalum are precipitated. The permissible degree of acidity that is consistent with total precipitation is very different with different elements. Thus with iron, titanium and zirconium it is surprisingly high; but relatively low with copper and thorium—it being almost necessary to use acetic acid in the latter cases. In addition to the above elements, which are quantitatively thrown down by cupferron under favorable conditions, the following are known to be either partially precipitated with or more or less occluded by the titanium precipitate: silicon (colloidal silicic acid), tungsten (tungstic acid), cerium (quadrivalent to a much greater extent than trivalent), silver, lead, mercury and bismuth. Most of these, however, may be readily removed by well known methods before applying the cupferron test; and further, since comparatively few of them are likely to occur in any given material, the number of serious interferences, as far as titanium is concerned, is not so great as might be supposed.<sup>120</sup> On the other hand, aluminum, beryllium, chromium, uranium (uranyl salts), manganese, nickel, cobalt, zinc, cadmium, platinum (chlorplatinic acid), alkaline earths, alkalis (including ammonium salts), phosphoric acid, arsenic acid and boric acid are not precipitated at all under the circumstances.

### Color Tests.

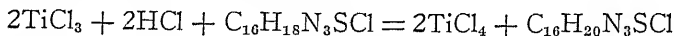
1. *Zinc* or *tin*, when added to a solution of a titanium salt containing hydrochloric acid, causes the gradual development of a violet color.



This reaction does not in itself constitute a particularly delicate test for titanium; but on further examination the reduced solution exhibits properties which are very conspicuous and rather characteristic of titanium.

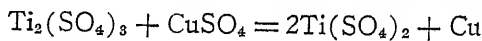


On adding the titanous chloride to a very dilute solution of methylene blue the color of the latter is promptly discharged, provided the temperature be not lower than 35°C. In this way it is possible to detect as little as 0.00001 gram of titanium.<sup>121</sup>



Indigotin may be substituted for methylene blue, provided some potassium sodium tartrate be added also.<sup>122</sup> Vanadium (bivalent), tungsten (quadrivalent), molybdenum (trivalent), chromium (chromous salts), tin (stannous salts) and copper (cuprous salts) behave similarly; but many metals, particularly iron (ferrous salts), do not interfere. Hydrogen sulfide and sulfurous acid reduce methylene blue to the corresponding leuco compound; while nitrous acid and arsenious acid are without effect.<sup>123</sup>

If a solution of titanous sulfate (free from chlorides) be added to a cold, dilute and slightly acid solution of copper sulfate, a finely divided red precipitate of metallic copper gradually makes its appearance.



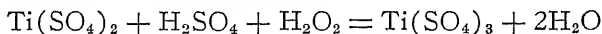
With very dilute solutions the color is blue by transmitted light though copper-red by reflected light. As a test for copper it is sufficiently delicate to detect 1 part of that element in 1,000,000 parts of solution.<sup>124</sup>

When a solution of titanic sulfate is reduced by zinc and sulfuric acid and added to a nearly saturated solution of mercuric chloride, containing also a little hydrochloric acid, no precipitation takes place at once; but after standing a considerable length of time a precipitate is slowly formed—difference from columbium, which immediately gives a precipitate.<sup>125</sup>

In the presence of hydrofluoric acid, the zinc and acid mixture produces a green coloration and not the usual violet as noted above. The assumption of Knecht and Hibbert<sup>126</sup> that the color is due to a double fluoride of potassium and titanium is probably erroneous. That it is caused by a fluoride of zinc and titanium seems more likely; since it may be obtained in the absence of potassium salts.

Certain other metallic elements, on reduction with zinc and acid, give colors similar to that of titanium. Columbium gives a dirty-blue coloration. Tungstic acid, in strong hydrochloric acid solution, changes first to blue, then becomes violet and finally yields a brown solution. Vanadic acid turns from orange to blue, blue to green and green to violet—each color corresponding to a definite valence. With the exception of columbium, interfering elements may be removed without much difficulty before applying the reduction test.

2. *Hydrogen peroxide*, on being added to an acidified solution of a titanium salt, produces an orange or yellow color according as the amount of titanium is large or small.<sup>127</sup>



E. Jackson<sup>128</sup> states that 0.00002 gram of titanic oxide in 1 gram of the solvent can be detected in this way; but R. C. Wells<sup>129</sup> finds the test to be much more sensitive, a very slight color being observable with only 0.0003 gram of titanic oxide in 100 cc. of the solution. Solutions deficient in acid do not show the maximum development of color;<sup>130</sup> hence, 5 cc. of sulfuric acid (sp. gr., 1.84) should be present for every 100 cc. of the solution.

Hydrofluoric acid<sup>131</sup> markedly bleaches the color, and phosphoric acid<sup>132</sup> and alkali salts<sup>133</sup> do so to a lesser extent.

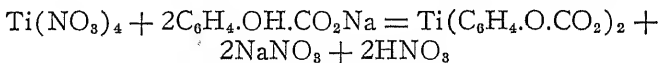
The following metals give distinct colors with hydrogen peroxide: chromium (violet), molybdenum (yellow) and vanadium (red-brown). The pale brownish yellow color of iron in sulfuric acid solution (free from chlorides) may be disregarded; but with hydrochloric acid solutions the iron should be separated from the titanium by extraction with ether before making the test.<sup>134</sup>

3. *Thymol*, in strong sulfuric acid, produces a beautiful garnet color, which fades off into reddish yellow with decreasing amounts of titanium.<sup>135</sup> The lowest strength of sulfuric acid that is consistent with complete development of color is 79.4 per cent (sp. gr., 1.725). The intensity of the coloration is said to be at least 25 times as great as that given by hydrogen peroxide.

Hydrofluoric acid destroys the color. Hydrochloric acid, phosphoric acid and tin are without effect. Tungstic and vanadic acids interfere.

Many organic substances give pronounced colors with titanium in concentrated sulfuric acid.<sup>136</sup> In this connection, L. Lévy<sup>137</sup> has shown that the crimson color produced by morphine may be used to differentiate titanium from columbium, tantalum and tin.

4. *Sodium salicylate* gives with a nearly neutral solution of a titanic salt a yellow precipitate in the cold, which is readily soluble in hot water.<sup>138</sup>



With small amounts of titanium an orange or yellow color is obtained, but no precipitate—a faint yellow being perceptible when only 0.00005 gram of titanic oxide is present in 100 cc. of the solution.<sup>139</sup>

Iron in the ferric condition must be absent; since it gives a purple color with salicylic acid. Columbium interferes slightly by imparting a

brownish color to the otherwise yellow solution. Zirconium and thorium give white precipitates, insoluble in hot water; while tantalum and certain of the rare earths are without influence upon the result.

5. *Hyposulfurous acid* gives with acid solutions of titanic chloride or sulfate an intense red color, which gradually grows yellow and finally disappears.<sup>140</sup>

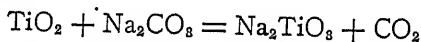
### High Temperature Reactions (Blowpipe Tests)

1. Titanium dioxide is chemically unaltered at the highest temperature of the blowpipe flame; but it assumes a temporary yellow color while hot, returning to its original nearly white color on cooling.

2. *Sodium ammonium phosphate* ("microcosmic salt") dissolves titanium compounds, after having been fused before the blowpipe and reheated in contact with the substance, giving a transparent glass. In the oxidizing flame, the bead is colored yellow while hot, if enough titanium be present, but becomes colorless on cooling. By prolonged application of the reducing flame, the bead, though still appearing yellow while hot, acquires a characteristic violet color on cooling.

The presence of much iron alters these results to a certain extent; but the violet color of the fully deoxidized bead is still pronounced.

3. *Sodium carbonate*, when fused with titanic oxide, converts it into sodium titanate.



On being leached with water, acidic titanates remain, and only a trace of titanium goes into solution.

If a little sodium nitrate be added to the flux, titanium may be separated from certain acid forming elements whose sodium salts are soluble in water, e.g., phosphorus, chromium, vanadium, molybdenum, etc.

4. *Sodium peroxide*, on being fused with titanic oxide, brings about the formation of sodium pertitanate. When the melt is extracted with water, the titanium goes into solution (difference from iron).<sup>141</sup>

### Microchemical Tests.

1. *Rubidium chloride*, on being added to a solution containing sodium fluotitanate, produces a white crystalline precipitate of rubidium fluotitanate ( $\text{Rb}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ ). The crystals exhibit a characteristic appearance under the microscope. The test is a very delicate one, it being possible to detect as little as 0.000001 gram of titanium.

Several substances, commonly associated with titanium, interfere, e.g., silicic and stannic acids, zirconium and aluminum.

2. *Potassium ferrocyanide* is also used as a microchemical reagent for titanium (cf. p. 57). This of course presupposes the absence of iron at the time of making the test.

For further information concerning the microchemical analysis of titanium see P. D. C. Kley.<sup>142</sup>

### Spectrographic Tests.

Titanium shows several conspicuous lines (p. 44), both in the arc and spark spectra, which may be used advantageously for purposes of identification; especially when small quantities of the element are present in substances of great complexity.

The spectrographic analysis of titaniferous materials will be dealt with to some extent in Chapter IX.

## Chapter IV.

# The Industrial Applications of Titanium and Its Compounds.

### (1) GENERAL CONSIDERATIONS.

Prior to 1900, the practical applications of titanium were few in number—the production of ore being confined to a very moderate amount of rutile that was used almost entirely for the glazing of pottery and in the manufacture of artificial teeth. It may be said then that the titanium industry is a comparatively young one, being certainly not more than twenty-five years old, if we reckon from the time when it began to assume a position of noteworthy importance.

Two developments, however, have created a very considerable demand for titanium, viz., the use of titanium alloys in metallurgy (more particularly, ferro-titanium in the treatment of iron and steel) and the introduction of titanic oxide into white composite pigments for painting, lacquering and similar arts. There is not so much ferro-titanium being used now as formerly; yet it may be said that this industry is holding its own. The production of pigment, on the other hand, is increasing rapidly and bids fair to become an enterprise of no contemptible magnitude.

Although most of the applications of titanium do not consume any great quantity of the element, still some of them are at least interesting in that they reveal a good deal of ingenuity on the part of the inventor. Accordingly, the uses are classified in Table III., the attempt being made to arrange them in descending order of their importance.

### (2) PIGMENTS.

#### Colored Pigments.

*Titanium Ferrocyanide.* The ferrocyanide of titanium is said to have been employed as a green pigment in lieu of the poisonous Schweinfurth green and other arsenical pigments.<sup>1</sup> It does not seem, however, that this pigment is on the market at the present time—certainly not to any great extent.

TABLE III.

## APPLICATIONS OF TITANIUM.

- 1    Pigments
- 2    Alloys in Metallurgy
- 3    Dyes, Mordants, Bleaching Agents, Strippers, Etc.
- 4    Refractory Materials (Glazes, Enamels, Glasses and Bricks)
- 5    Smoke Screens and Pyrotechnics
- 6    Incandescent Media for Lighting Purposes (Arc Lamp Electrodes, Etc.)
- 7    Cement
- 8    Gem Stones (Natural and Synthetic)
- 9    Abrasives
- 10   Catalysts
- 11   Ink
- 12   Medicinal Preparations
- 13   Nitrogen Fixation (Fertilizers)
- 14   Phosphorus Pentoxide
- 15   Applications in Pure Science

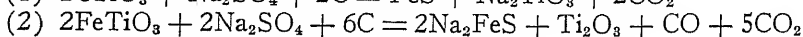
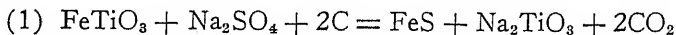
*Oxidized Ilmenite.* P. Farup<sup>2</sup> has patented processes for the manufacture of colored pigments which depend upon roasting highly titaniferous iron ores in a state of fine subdivision at not too high a temperature either alone or in admixture with sulfuric acid. The resulting product is in the former case of a reddish color while in the latter it is inclined to yellow. It is claimed by the inventor that the yellow pigment is especially useful in the preparation of rust-preventing paints, and that the color produced is lighter than was hitherto obtainable with paints of this character. However, G. Jebsen<sup>3</sup> has announced that these pigments did not prove to be economically successful.

### White Pigments.

*Preliminary Remarks.* The high refractive index of titanium dioxide (p. 49) has more to do with its fitness for use as a paint pigment than any other property. Although this fact has long been known, as well as other desirable qualities, its successful utilization for this purpose was not realized until within the last few years. In fact, it would not have been commercially possible to use pure titanic oxide alone in competition with other white pigments, unless some method of manufacture could have been discovered that would be cheaper than any now known. Fortunately, a composite pigment, prepared under certain special conditions, and containing only about one fourth of its weight of titanium oxide (the rest being an extender such as barium sulfate), has nearly the same covering power when spread in the form of paint as the oxide alone. Working along these lines, two organizations, viz., the Titanium Pigment Company, Inc. of Niagara Falls, New York and the Titan Co. A/S. of Christiania, Norway, have independently arrived at much the same goal.

*Manufacture of Titanium White ("Titanox")—Process of the Titanium Pigment Company, Inc.* In accordance with letters patent granted to A. J. Rossi and L. E. Barton <sup>4</sup> and subsequently to Barton, <sup>5</sup> "titanox" is produced in the following manner:

Ilmenite, <sup>6</sup> containing about 52 per cent of titanic oxide, is mixed with "niter cake" <sup>7</sup> and petroleum coke in the proportions: 100 parts of ore, 300 parts of "niter cake" and 50 parts of coke. This mixture is charged into an electric furnace and the whole thoroughly melted together. The following reactions are assumed to take place.



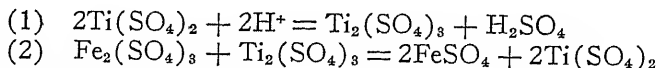
Equation (1) represents the predominant reaction and equation (2) a secondary reaction which occurs to a very much less extent.

The melt is then cast into deep molds in order that it may cool slowly, thus effecting a pretty fair separation into two layers by gravity. The upper portion (sp. gr., 2.75), consisting chiefly of ferro-sodium sulfide, is called the "matte", while the lower portion (sp. gr., 3.09), which contains most of the titanium as sodium titanate, is called the "titanium concentrate". It is now feasible to break away nearly all of the matte, leaving the titanium concentrate comparatively free from iron.

This material is lixiviated and the residue treated with dilute sulfuric acid (not over 20 per cent) at the boiling temperature, the acid being used in regulated quantity. These operations remove most of the impurities and bring about complete hydrolysis of the sodium titanate to titanic acid (or basic titanic sulfate) without causing any appreciable loss of titanium. The undissolved residue is separated from the supernatant liquid by a suitable method, such as decantation or filtration, washed and dried (but not calcined).

This concentrate dissolves readily in strong sulfuric acid. <sup>8</sup> To this end it is treated with from 2.5 to 2.6 parts of 95 per cent acid in an iron vessel and digested at a temperature of 100°C. to 150°C. The mass is then transferred to a lead lined tank and diluted with water, the volume of which should be about three times that of the sulfuric acid previously used. All dissolves except a relatively small amount of unattacked matter. The solution is clarified by filtration and placed in an appropriate vat for the next step in the process.

A small fraction of the solution, a little more than enough to react with all remaining iron, is temporarily removed from the bath and deoxidized by means of the electric current. On returning this to the main solution, the titanous sulfate reduces the ferric sulfate to ferrous sulfate, the latter having much less tendency to yield a precipitate by hydrolysis.



Meanwhile a finely divided, or sponge-like, precipitate of barium sulfate is prepared by heating together a mixture of barytes and coke, extracting the barium sulfide with water and adding sodium sulfate thereto.

The filtered and washed barium sulfate is added to the titanic sulfate solution in the form of pulp—the amount to be introduced being calculated from a knowledge of the composition of the solution and pulp respectively. The mixture is then heated and thoroughly agitated; whereupon the titanic sulfate is decomposed and the resulting compounds (basic titanic sulfate and titanic acid) adhere to, coalesce with and impregnate the dispersed aggregations of barium sulfate particles. The composite mass is separated by filtration, washed, dried and calcined in a rotary kiln. It is then ready for use in the manufacture of paint.

*Manufacture of Titanium White Continued—Process of the Titan Co. A/S.* The Norwegian process, as described by Jebsen,<sup>9</sup> differs from the American in several respects.

The finely pulverized titaniferous ore, containing about 42 per cent of titanium dioxide, is thoroughly mixed with sulfuric acid and the two are heated together until the conversion of titanium and iron to sulfates is practically complete. The resulting cake is crushed to powder and extracted with water. The unattacked mineral is allowed to settle, after which the clear fluid is drawn off. The solution is then subjected to electrolysis until the iron is fully reduced from the ferric to the ferrous condition without, however, causing the reduction of any very great quantity of the titanic salt (see above). On heating the solution, thus deoxidized, the titanium is precipitated free from iron as a white amorphous powder. The washed product contains some sulfuric acid, but it is otherwise free from impurities. It is therefore treated with a sufficient quantity of barium carbonate to neutralize the acid, and the mixture is calcined at a suitable temperature. This product is pulverized to a state of excessive fineness, ground in linseed oil along with some zinc-white and the paste so produced is sold to the trade.

Another innovation is the addition of calcium phosphate to the titanium precipitate after treatment with barium carbonate. After leaving the furnace, the pigment contains about 10 per cent of phosphorus pentoxide. This is said to produce a pigment of exceptional whiteness.<sup>10</sup>

*Properties and Uses of Titanium White ("Titanox").* "Titanox", which contains almost exactly 25 per cent of titanium dioxide and 75



per cent of barium sulfate, is a very fine, uniform, white powder and extremely smooth to the touch. Its specific gravity is 4.3, whence the bulking figure <sup>11</sup> 35.8 is obtained. The oil required for grinding it to a paste is about 17 per cent. It is chemically stable, inert toward such gases and vapors as are likely to be present in the atmosphere, does not react with paint vehicles, i.e., does not saponify the oil, is not altered by light and even withstands a high baking temperature without discoloration. Although "titanox" is inferior to pure titanic oxide in hiding power for any given degree of brightness (coefficient of diffuse reflection), it is markedly superior in this respect to all of the better known white pigments.<sup>12</sup>

In the manufacture of paint "titanox" is employed in much the same manner as other pigments. It is first ground in linseed oil to a paste, after which it is diluted to the proper consistency with more oil <sup>13</sup> and the thinner and drier are added in suitable proportions. When used on outside work, paints containing "titanox" as the only pigment dry to a film that is somewhat too soft to resist the accumulation of dust particles. Moreover, these paints chalk moderately. If, however, zinc oxide to the extent of from 20 to 30 per cent of the aggregate weight of the pigments for white paints and from 40 to 50 per cent for tinted paints be added, both the discoloration by dust and the tendency to chalk are very largely prevented. It is also stated that the addition of a small quantity of asbestine (up to 20 per cent of the pigment formula), owing to the angularity of its particles, improves the brushing quality of the paint.<sup>14</sup> Surfaces painted with "titanox", to which the proper amount of zinc oxide has been added, do not check, crack or scale on long exposure and invariably present a good foundation for repainting.

"Titanox" works well in flat wall paints; but for this purpose the addition of zinc oxide is unnecessary.

In the preparation of enamels, "titanox" has been introduced in very noteworthy amounts. Such enamels have great covering power, and may be baked at a higher temperature than was formerly permissible.<sup>15</sup>

Furthermore, "titanox" has been used with good results in the manufacture of lacquer, printing ink, wall paper, rubber, oil-cloth, linoleum, roller shades, etc. Indeed, it is impossible to say into which of the useful arts this excellent pigment may not sooner or later find its way.<sup>16</sup>

### (3) ALLOYS.

#### Ferro-Titanium.

*Preliminary Remarks.* Since it was known, at a comparatively early date, that the smelting of certain titaniferous iron ores yielded metal

of excellent quality, it naturally occurred to investigators that the titanium originally present might have some beneficial effect on the product. As early as 1901, and perhaps sooner, Rossi<sup>17</sup> seems to have been aware that titanium, when added to steel in the form of ferro-titanium, is capable of bringing about certain desirable results; and, since in some cases analyses of titanium-treated steels showed little or no residual titanium, he was inclined to think that the improvement was due to some indirect action on the part of the titanium and not to an ordinary alloying effect. This supposition has since been fully confirmed by many experiments—it being now well known that the beneficial action of ferro-titanium, when added to iron or steel in the molten condition, depends upon the fact that at high temperatures titanium has a very strong tendency to combine with both oxygen and nitrogen to form stable oxides and nitrides, which rise to the surface and are removed with the slag, thus sweeping the metal free of air vesicles (or from these gases otherwise held) and at the same time preventing segregation. Hence the ingots or castings show greater soundness, cleanness and freedom from segregated impurities as compared with the untreated steel.

Several other metals exert a similar purging action, and the relative merits of these along with titanium have been summarized by B. Stoughton<sup>18</sup> in the following manner:

Prevention of blowholes: (1) aluminum, (2) titanium, (3) silicon, (4) vanadium, (5) manganese.

Removal of oxides of iron and manganese: (1) titanium, (2) silicon (weakly). Hindering this removal: (1) aluminum, (2) manganese.

Removal of all oxides and slag enclosures: (1) titanium. Hindering removal of all these enclosures: (1) aluminum.

Removal of nitrogen: (1) titanium, (2) vanadium (?).

Breaking up and removal of iron sulfide: (1) manganese, (2) titanium.

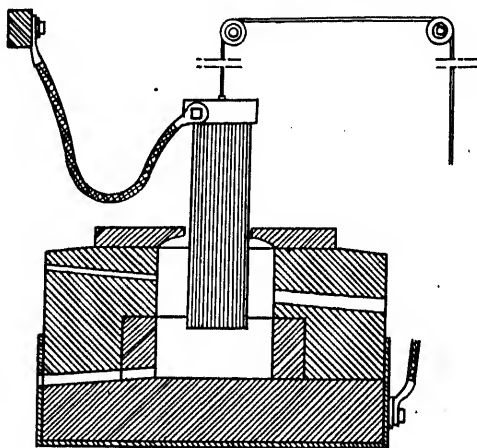
Causing a pipe: (1) aluminum, (2) silicon, (3) titanium, (4) vanadium, (5) manganese.

Hindering segregation: (1) aluminum, (2) titanium, (3) vanadium.

Promotion of segregation: (1) manganese, (2) silicon (sometimes).

Although titanium compares favorably with the other above corrective agents in all respects, it is especially noteworthy that it stands pre-eminently first as a remover of nitrogen.<sup>19</sup> Moreover, it does not leave any objectionable residue, as does aluminum, and it facilitates the removal of silicate inclusions by acting as a flux. Zirconium also acts as a scavenger;<sup>20</sup> but owing to its greater cost it will probably not replace titanium to any noticeable extent.

*Manufacture of Ferro-Carbon-Titanium—Process of the Titanium Alloy Manufacturing Company.* In accordance with patented processes by Rossi,<sup>21</sup> titanium ore, scrap iron and coke are mixed together in the proper proportions and charged into an electric furnace of special design (Figure 10). This furnace is peculiar in having only one electrode—the hearth and a small part of the wall being composed of a conducting substance, such as graphite, the rest of the lining being a non-conducting and sufficiently refractory material. The current is so regulated as to maintain the necessary temperature (about 3,500°F.), and as soon as the reactions are complete the metal is tapped at the bottom vent. From 600 to 1,000 pounds are obtained at each run. There is almost



(U. S. Patent, No. 802,941, Oct. 24, 1905.)

FIG. 10.—A. J. Rossi's furnace for making ferro-titanium.

no slag, and such small amounts as are obtained are returned to the furnace with another charge. The material is then broken, crushed and screened—it being sold to the trade in different sizes according to the purpose for which it is intended.

*Manufacture of Ferro-Titanium (Carbon-Free)—Process of the Titanium Alloy Manufacturing Company.* A ferro-titanium very nearly free from carbon may be produced by a method similar to that already given for ferro-carbon-titanium with the exception that the reduction is accomplished by means of a bath of molten aluminum.<sup>22</sup> The Titanium Alloy Manufacturing Company, however, has found it more satisfactory to specialize in the carburetted alloy; consequently little or none of the carbon-free material is being produced by this organization at the present time.

*Manufacture of Ferro-Titanium (Carbon-Free) Continued—Aluminothermic Process.* Ferro-titanium is being manufactured by the Metal and Thermit Corporation<sup>23</sup> in accordance with the general method of H. Goldschmidt, whereby the metal may be obtained from many difficultly reducible oxides.<sup>24</sup> A mixture of iron and titanium oxides (practically speaking, ilmenite) and aluminum, all in the state of fine powder, are thoroughly commingled. Then, by means of a fuse, some point within the mixture is raised to the ignition temperature; whereupon the aluminum combines with the oxygen, the reaction being almost instantaneous with evolution of much heat and light. In order to get the reaction well started, it is customary to surround the fuse (magnesium ribbon) with a priming charge consisting of aluminum powder and barium peroxide. All metals prepared by the thermite process contain more or less aluminum alloyed with them; but they are practically free from carbon.

*Composition, Properties and Uses of Ferro-Titanium.* The chemical composition of the two important varieties of ferro-titanium is shown by the average analyses of Table IV.

TABLE IV.  
TYPICAL ANALYSES OF FERRO-TITANIUM.

	F.-C.-T. <sup>a</sup>	F.-T. (Thermite) <sup>b</sup>
Ti .....	15.79 per cent	25 per cent
Fe .....	74.30 " "	67.44 to 68.94 " "
C .....	7.46 " "	nil
Si .....	1.41 " "	1 to 1.5 " "
Al .....	0.08 " "	5 to 6 " "
Mn .....	0.11 " "	nil
S .....	0.08 " "	0.01 " "
P .....	0.05 " "	0.05 " "

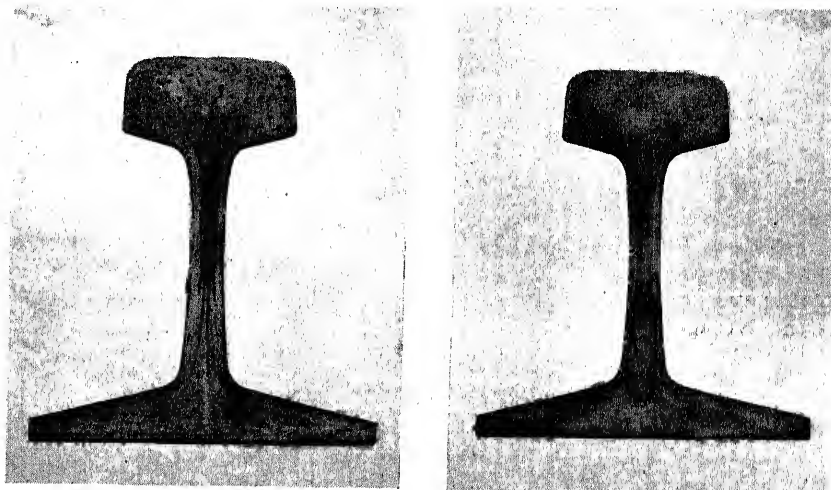
<sup>a</sup> Anon.: Ferro Carbon Titanium in Steel Making, 1919, p. 5. The Titanium Alloy Manufacturing Co., Niagara Falls, N. Y.

<sup>b</sup> Robinson: Can. Dep. Mines, Mines Branch, No. 579, 100 (1922).

Ferro-carbon-titanium is a dark iron-gray scoriaceous mass; carbon-free ferro-titanium, whether made in the electric furnace or by the aluminothermic process, is more compact and of a pleasing silvery appearance.

Either variety of titanium alloy is used as the final deoxidizer and denitrogenizer in the manufacture of steel—other ferro-alloys, such as ferro-manganese, or spiegeleisen, ferro-silicon, etc., having been previously added. It is put into the ladle while the steel is being poured (before the slag has begun to run), and the ladle is held for a few minutes before teeming into ingots. The amount of ferro-titanium to

be added varies considerably according to the kind of steel that one wishes to produce. For open-hearth structural steel, about 0.03 per cent of titanium (in the form of ferro-carbon-titanium) is used and practically no titanium remains in the final product. With thermit ferro-titanium, from 0.5 to 1 pound of alloy is added for every ton of steel. For rail steel, however, ferro-carbon-titanium should be added to the extent of 13 pounds per ton (0.1 per cent of metallic titanium).



(*Rail Reports—Open Hearth, Bull. 3, pp. 14-5, 1918. Titanium Alloy Manufacturing Co.*)

FIG. 11.—Etched section of untreated A rail (left) and titanium treated A rail (right).

Titanium-treated steels are said to be denser, closer grained and free from blow holes and pin holes. The pipe is reduced in size, and segregation (especially of carbon, phosphorus and sulfur) is very largely eliminated. Castings are not brittle, heat less under the tool and may therefore be machined more rapidly than other steels of equal carbon content. Titanium treatment raises the elastic limit of steel, and increases its tensile strength as well as its elongation and contraction.

The beneficial effects of titanium in steel metallurgy have been shown to be very pronounced in the manufacture of Bessemer rails, concerning which W. C. Brown,<sup>25</sup> formerly president of the New York Central Lines, has commented most favorably. The manufacture of these rails had its heyday in 1910, 256,759 gross tons of rail steel being produced during the year; but since then it has undergone a very decided falling off. This is due to the ascendancy of the open-hearth process in making steel for rails, which, on account of its mechanical superiority to

Bessemer steel, renders titanium treatment less necessary. However, the fact remains that it is possible to make still better steel if titanium is used in connection with the open-hearth process also.<sup>26</sup>

Titanium is used extensively in the making of sheet steel for galvanizing<sup>27</sup> and tin plating.<sup>28</sup> It is used in the production of high grade structural steels, e.g., automotive steels, and in making certain alloy-steels it has been proven to be of especial value. During the recent war, the partial substitution of titanium for manganese, with a view to conserving the latter metal, was successfully carried out at several plants.<sup>29</sup>

Titanium may be added to cast-iron with certain desirable effects, as Stoughton<sup>30</sup> and R. Moldenke<sup>31</sup> have shown.

The addition of larger amounts of titanium to steel, so as to produce a true alloy-steel, is still an open question. At the present time, however, the weight of opinion favors the conclusion that such steels have no peculiar value.<sup>32</sup>

### Cupro-Titanium and Mangano-Titanium.

Titanium-copper, containing 10 per cent of titanium, and manganese-titanium, containing 30 per cent of titanium, are now being manufactured by the Metal and Thermit Corporation. It is also interesting to note that Rossi<sup>33</sup> has patented processes for the preparation of similar alloys in the electric furnace. The Titanium Alloy Manufacturing Company, however, is not producing any alloys of titanium and the non-ferrous metals at the present time. These alloys must be kept as free from iron as possible; hence rutile and not ilmenite is used as the ore.

Both cupro-titanium and mangano-titanium are used as deoxidizers in making brass and bronze castings. The metals are said to be improved by such treatment because of the cleansing effect of the titanium in much the same way that steel is benefited by the addition of ferro-titanium. Manganese-titanium is also used as a scavenger for certain white metal alloys and especially for alloys of nickel and chromium.<sup>34</sup>

### Other Alloys.

A good many alloys of titanium with various other metals have been prepared, and in some cases the processes have been patented; but as far as is known to the author at the time of writing, none of these has thus far turned out to be of much importance. Titanium-bearing aluminum alloys, however, are said to have been manufactured by the Aluminum Manufactures, Inc. of Cleveland, Ohio on a commercial scale.<sup>35</sup> Furthermore, M. A. Hunter and J. W. Bacon<sup>36</sup> have studied some of the electrical properties of certain titanium alloys and in a few cases report promising results.

## (4) DYES, MORDANTS, BLEACHING AGENTS, STRIPPERS, ETC.

As early as 1885 J. Barnes<sup>37</sup> called attention to the fact that salts of titanium could be used advantageously in mordanting yarn. For this purpose he employed a solution of titanous chloride to which some sodium acetate had been added, and obtained pleasing colors on the cloth with alizarin and other dyestuffs. Since then various compounds of titanium have found favor in the textile industry for the fixation of color on the fabric. Among these may be mentioned the tartrate,<sup>38</sup> tannate,<sup>39</sup> double sulfate,  $\text{Na}_2\text{TiO}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,<sup>40</sup> double oxalate,  $\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ,<sup>41</sup> etc.

Besides serving as a good mordant for basic dyestuffs, titanium tannate in oxalic acid solution (tanno-oxalate) produces yellow and golden shades on the cloth, particularly on mercerized cotton,<sup>39</sup> thus acting as a dye itself.

Titanium, in the form of tartrate or tannin-titanium, has been applied in calico printing.<sup>38</sup>

In 1901 E. Knecht suggested the use of the titanous salts as stripping agents. To this end the chloride,  $\text{TiCl}_3$ ,<sup>42</sup> and double sulfate,  $\text{Na}_2\text{Ti}_2(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$ ,<sup>43</sup> are generally employed. The two best strippers of reducing character, as pointed out by E. Hibbert,<sup>44</sup> are titanous chloride, which acts in an acid bath, and a combination of formaldehyde and sodium hydrosulfite, which is used in an alkaline solution. Titanous salts are also said to be good bleaching agents.

Titanium compounds are used on a rather extensive scale in the leather industry. The most important salt is the oxalate of titanium and potassium. When vegetable tanned leathers are to be dyed with basic coloring matters, the potassium titanium oxalate, like tartar emetic, serves the double purpose of acting as a mordant and of precipitating any free tannin that might otherwise diffuse into the bath and throw down the dyestuff.<sup>45</sup> Titanium salt is used as a striker with logwood to produce black, and is said not to embrittle the leather, as do salts of iron. It may also be used alone to produce on the fiber a yellowish-brown color due to titanium tannate, which is permanent and especially suited to shoe leathers.

Knecht<sup>46</sup> has taken out patents for a cellulose solvent, which is prepared by dissolving very finely divided metallic copper in ammonium hydroxide in the presence of air. Copper in sufficiently small particles for the purpose is produced by the addition of a powerful reducing agent, such as titanous sulfate or chromous sulfate, to a solution of copper salt (cf. p. 60). The solution of cellulose so obtained is claimed to be suitable for making fibers, films, etc.

## (5) REFRACTORY MATERIALS (GLAZES, ENAMELS, GLASSES AND BRICKS).

The purer grades of rutile are used to impart a beautiful, soft yellow, under-glaze color to pottery. Titanium is indeed one of the comparatively few substances that can be used for under-glaze painting in the decoration of porcelain, the effects so obtained being in many ways superior to those gotten by painting upon the glaze. As a yellow ceramic pigment titanic oxide is much less expensive than oxide of uranium and admits of greater variation in shade than does oxide of iron. It may also be used in admixture with other substances—thus giving the manufacturer greater latitude of choice as to the possible tone of color that may be produced. Great care is necessary in the firing; for in contact with reducing gases titanium gives objectionable off-colors (copper-red or blue).<sup>47</sup>

Rutile is likewise used in making artificial teeth, for which purpose the amount added to the paste varies from 0.5 to 5 per cent according to the color desired. Dental enamels put out by the Foote Mineral Company of Philadelphia, Pa. are said to contain titanium compounds.<sup>48</sup>

Titanium dioxide acts as a crystallizer for producing crystalline glazes on art pottery, there being but few bodies known that have this property.<sup>49</sup>

When added in certain proportions titanic oxide develops opacity in enamels, the colors being chiefly grayish-white or yellowish-white.<sup>50</sup> Titanium enamels have been experimentally studied by R. D. Landrum and L. J. Frost,<sup>51</sup> who report that, although there are some technical difficulties yet to be overcome, it should be possible to develop them to a point of real practical value. Such enamels are chemically inert, resistant to abrasion and capable of withstanding high temperatures.

Under the name "siloxide", F. Thomas<sup>52</sup> has described a substitute for vitreous quartz, which is made by adding a small quantity of either zirconium or titanium oxide or both to silica. The glasses contain from 0.5 to 2 per cent of zirconium or titanium, though 1 per cent gives the best result. These glasses are in some respects mechanically better than fused quartz, are more resistant toward substances of alkaline nature and have a greater viscosity at high temperatures. They can be worked in the oxyhydrogen flame. The titanium glass is blue in color; but otherwise it resembles closely the zirconium glass, resisting devitrification even better than the latter. "Siloxide" was being manufactured by the Zirkonglasgesellschaft m. b. H., Frankfurt a/M. in 1912.

Titanic oxide (melting point, 1560° C.) is used in the making of bricks and ilmenite as a constituent of the lining of puddling furnaces.



## (6) SMOKE SCREENS AND PYROTECHNICS.

Among those materials that have been used for the production of smoke clouds for the concealment of military or naval operations, titanic chloride, because of chemical similarity, may best be compared with the tetrachlorides of silicon and tin. There being no commercially workable tin deposits in the United States, titanium chloride would doubtless be the more readily available of the two in times of war as far as this country is concerned. On the other hand, silicon is of almost ubiquitous occurrence and the supply is practically unlimited. As far as American developments had gone in 1919, silicon chloride had become much more important than titanium chloride, and tin chloride, though less available, had proven more satisfactory for grenades than the corresponding titanium compound. However, titanium tetrachloride has some properties that would seem to render it valuable as a smoke producer, and the failure to obtain better results with it may have been due to inadequate projecting apparatus as much as to any inherent deficiency on the part of the substance itself.

Titanic chloride is a liquid with a comparatively high boiling point ( $136.4^{\circ}\text{C.}$ ),<sup>53</sup> which fumes strongly on exposure to ordinary air. If, instead of allowing a given quantity of the liquid to evaporate slowly, it be suddenly dispersed by means of an explosive charge, a much larger smoke cloud is produced which persists for a correspondingly shorter period of time. The fuming of the chloride is due to two reactions: a hydrate,  $\text{TiCl}_4 \cdot 5\text{H}_2\text{O}$ , is first formed, which with excess moisture is hydrolyzed to hydrochloric acid and titanic acid, and the obscuring power of the hydrate is greater than that of the mixture of hydrolytic products. Furthermore, if ammonia gas be added, the cloud is considerably intensified owing to the formation of ammonium chloride. For the best results the following conditions are necessary: liquid ammonia and the chloride are sprayed into the atmosphere in an atomized state, both components are largely diluted with air before mixing and enough moisture is present to complete the hydrolysis of the chloride before it comes into contact with the ammonia. Unless the third condition be fulfilled, an additive compound with ammonia,  $\text{TiCl}_4 \cdot 6\text{NH}_3$ , is formed, which is broken down but slowly and which lowers the obscuring power of the cloud.

Silicon tetrachloride displays similar properties, but it hydrolyzes directly and promptly. Because of its greater volatility it is much better suited to being sprayed through nozzles, such as are used in the Navy Smoke Funnel, than titanic chloride; since it does not cause clogging. In brief, the general efficiency of the silicon compound is greater, in spite of the fact that the hiding power of the titanium

analogue—both being mixed with ammonia—is about 50 per cent higher.

For use alone (without ammonia) in shells neither chloride is of much avail. In average weather the titanium cloud is better; but with high humidity silicon has the advantage.<sup>54</sup>

Titanium tetrachloride is being used, however, in the airplane exhaust smoke and the airplane curtain because it is the most desirable for that purpose.<sup>55</sup>



(Courtesy of Mr. D. B. Bradner of the U. S. Arsenal, Edgewood, Maryland.)

Fig. 12.—Titanium tetrachloride smoke screen.

C. Baskerville<sup>56</sup> states that titanium has been employed in pyrotechnics because of the beautiful light that it produces during combustion; but he gives no further details.

#### (7) INCANDESCENT MEDIA FOR LIGHTING PURPOSES.

One of the most remarkable applications of titanium is the use of its compounds, dioxide, suboxide or carbide, in arc lamp electrodes. As stated by I. Ladoff,<sup>57</sup> among all the metals titanium possesses the highest point of electrovaporization and furnishes the richest spectrum as far as the number of lines is concerned. Moreover, W. S. Weedon<sup>58</sup> found that, of the many substances tried for prospective use in arc light electrodes, those containing titanium gave the highest efficiency in candle power per watt consumed.

In accordance with patents granted to J. T. H. Dempster,<sup>59</sup> the General Electric Company of Schenectady, N. Y., manufactures an electrode in which titanium oxide is the chief light-giving material. There is a good deal of variation indicated in the patent specifications

as to the nature of the substances used and the way in which they are incorporated into the electrode mass; but the following example will serve to give an idea of their composition. A mixture of 70 parts of magnetite, 30 parts of rutile and 15 parts of chromic oxide (or some material containing chromic oxide such as the mineral chromite) is packed into a cylindrical tube of sheet iron. In the above composition the iron of the magnetite is the base or foundation which primarily furnishes and feeds the arc, the titanium serves to intensify the luminosity and the chromium retards the consumption of the electrode. This constitutes the negative electrode only. The composition of the positive electrode is immaterial; though it should be made non-consuming by giving it a large enough size to keep cool. As pointed out by C. P. Steinmetz,<sup>60</sup> in this type of arc, which is called "luminous," the light is not a temperature effect; but corresponds more nearly to a direct conversion of electrical energy into light.

The present industrial status of the titanium arc is embodied in the following statement by E. R. Berry: "While it is no doubt true that the luminous arc lamp has certain operating difficulties which are not shared by the nitrogen filled tungsten lamp, it is not true that the latter lamp supplanted the arc lamp, as there are at the present time about 300,000 of these lamps in use. Owing to the superior quality of the light, the luminous arc lamps are still proving very desirable units for certain types of street lighting".<sup>61</sup>

Titanium dioxide has been tried as a component of gas mantles; but it has been shown to be unsatisfactory.<sup>62</sup>

A certain amount of experimenting has been done with a view to obtaining a filament of metallic titanium for incandescent electric lamps; but it does not seem that such lamps were ever placed on the market.

#### (8) CEMENT.

E. C. Eckel,<sup>63</sup> in a patented process, claims that a quick-hardening and chemically resistant cement may be obtained as a by-product in the smelting of titanic iron ores in either the blast or electric furnace using limestone as the flux. With proper adjustment of the ingredients of the furnace charge, the slag consists essentially of calcium titanate,  $\text{CaTiO}_3$ , with subordinate amounts of ferrites, aluminates and silicate of calcium. This slag, when finely ground, constitutes a cement that within 24 to 48 hours will attain a higher degree of strength than Portland cement under the same conditions. Reasonable amounts of magnesia may replace a part of the lime, but too much magnesia is objectionable.

## (9) GEM STONES

## Natural Stones.

Clear crystals of rutile are occasionally cut to give gems of red color, and the dark variety (known as nigrine) yields a stone that resembles the black diamond in appearance. Inclusions of fine rutile crystals in transparent quartz constitute the stone which is perhaps best known by the sentimental name of "*flèches d'amour*" (love's arrows). When cut *en cabochon* this material affords an odd and attractive gem. Elegant rutile has come from Graves Mountain, Georgia, and both rutile and sagenite of fine quality have been found in some quantity in Western North Carolina.<sup>64</sup>

Beautiful blue crystals of octahedrite (polymorphous with rutile) have come from Brazil and small pale-green crystals from North Carolina.

The mineral titanite, or sphene, because of its high refractive index, yields a stone having a good deal of sparkle when cut in the form of a brilliant. The color is usually a light shade of yellow or green. It is too soft (hardness, 5 to 5.5), however, to stand constant wear when set in jewelry.

Benitoite, first described by G. D. Louderback,<sup>65</sup> occurs in San Benito County, California. It is fairly hard (6.25 to 6.5) and has a pleasing blue color. It is said to resemble the sapphire in appearance.

O. C. Farrington<sup>66</sup> mentions polycrase, along with a number of other rare minerals, which when cut and polished make brilliant black gems.

## Synthetic Stones.

A. V. L. Verneuil,<sup>67</sup> who successfully synthesized the ruby, has also prepared sapphires by fusing together with an oxyhydrogen torch of special construction a mixture consisting of 98 per cent of aluminum oxide, 1.5 per cent of iron oxide and 0.5 per cent of titanium oxide.<sup>68</sup> The resulting pear-shaped globule represents a single crystal of alumina, which when cut and polished is practically identical with the natural sapphire.

The synthetic ruby can be made by virtually the same process, the red color being obtained by introducing a small quantity of oxide of chromium.

These stones are in no sense to be regarded as imitations; since they possess both physical and chemical properties that are the same as those of the earth-made gems except for a few minute structural differences that are revealed only by the high power microscope.

In 1913 I. H. Levin<sup>69</sup> stated that 10,000,000 carats of rubies and 6,000,000 carats of sapphires were being produced annually and that the demand was increasing.

#### (10) ABRASIVES.

T. L. Watson and G. Steiger<sup>70</sup> have described a titaniferous emery occurring in Pittsylvania County, Virginia, that is claimed to have commercial value as an abrasive. The rock is made up of the minerals ilmenite, magnetite, corundum and spinel.

The nitride of titanium,  $Ti_2N_2$ , which was prepared by H. Moissan<sup>71</sup> in the electric furnace, is said to be an extremely hard substance.

Patents have been granted to L. E. Saunders<sup>72</sup> for the manufacture of an abrasive material in the electric furnace, which, though essentially aluminous, contains also noteworthy amounts of ferric oxide, titanic oxide, silica and lime.

#### (11) CATALYSTS.

P. Sabatier<sup>73</sup> mentions the use of titania as a catalyst in the preparation of a good many types of organic compounds and also in the cracking of petroleum. To obtain an active form of titanium oxide, the hydroxide is precipitated by adding ammonium hydroxide to a solution of titanic chloride, which in turn is dehydrated at a temperature below  $350^{\circ}C$ .<sup>74</sup> Recent work by H. Adkins and A. C. Krause,<sup>75</sup> however, goes to show that the action of the three substances, alumina, titania and thoria, in catalyzing the decomposition of certain acetic esters is not so specific as Sabatier had originally supposed and that the result obtained depends quite as much upon the manner of preparing the catalyst as upon the particular metallic element present in the oxide.

F. W. Attack<sup>76</sup> has patented a process for the oxidation of aromatic hydrocarbons with titanic oxide as the catalyst. The organic substance in the state of vapor and admixed with air or oxygen is passed over the catalyst, which may be supported on a carrier (such as brick, asbestos or pumice). It is claimed that in this way anthracene may be oxidized to anthraquinone and naphthalene to phthalic acid and phthalic anhydride.

#### (12) INK.

The compound formed between titanium and logwood (p. 74) has a deep black color and may therefore be used as an ink. It is described as being a permanent fluid that undergoes no change after being used.<sup>77</sup>

The use of "titanox" in printing inks has already been mentioned (p. 68).

## (13) MEDICINAL PREPARATIONS.

The therapeutic applicability of titanium compounds is very limited and unimportant. J. Pick<sup>78</sup> has used certain salts of titanium, especially the sulfate and salicylate, as local remedies in the treatment of eczema, lupus, rhinitis and conjunctivitis, and claims to have obtained beneficial results. He asserts further that all inorganic and organic titanium compounds, provided they are soluble in water, check the putrefaction of protein and that the salts are not poisonous when taken internally.

## (14) NITROGEN FIXATION.

Owing to the readiness with which titanium combines with nitrogen (pp. 44 and 69), and with carbon and nitrogen to give the cyanonitride, a good deal of experimenting has been done with a view to utilizing these reactions for the fixation of atmospheric nitrogen. According to patents by C. Bosch,<sup>79</sup> assignor to the Badische Anilin- und Soda-Fabrik, compounds between titanium and nitrogen are rapidly formed when a mixture of titanic oxide and charcoal is heated in the presence of an alkali salt at about 1,240°C., the action of the alkali compound being apparently catalytic. The titanium-nitrogen compounds by simultaneous oxidation and hydrolysis can be made to yield ammonia, and in the presence of platinum more or less of the ammonia is converted into oxide of nitrogen.<sup>79</sup> The following equations will serve to illustrate some of the possible reactions:

- (1)  $2\text{TiO}_2 + 2\text{C} + \text{N}_2 = \text{Ti}_2\text{N}_2 + 2\text{CO}_2$
- (2)  $\text{Ti}_2\text{N}_2 + 4\text{NaOH} + \text{H}_2\text{O} + 2\text{CuO} = 2\text{NH}_3 + \text{Cu}_2\text{O} + 2\text{Na}_2\text{TiO}_3$   
—autoclave at 180°C.
- (3)  $2\text{Ti}_2\text{N}_2 + 2\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} + \text{O}_2 = 4\text{TiO}_2 + 2(\text{NH}_4)_2\text{SO}_4$ —autoclave at 120°-140°C.
- (4)  $2\text{Ti}_2\text{N}_2 + 7\text{O}_2 = 2\text{N}_2\text{O}_3 + 4\text{TiO}_2$ —current of mixed air and steam at 300°-400°C. in presence of platinum

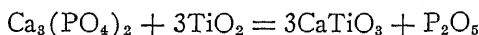
More recently, F. v. Bichowsky and J. F. Harthan,<sup>80</sup> working along similar lines, have secured patents on improved procedures for the preparation of titanium-nitrogen compounds. The chief novel feature of these processes would seem to be the introduction of iron as an additional catalyst in reaction (1) above, which lowers the operating temperature to about 1,000°C. They also claim that the residue gives ammonia when heated with soda-lime and that the action of superheated steam at about 700°C. causes the formation of both ammonia and hydrocyanic acid mixed with some hydrogen.

These inventions, though interesting, have thus far not been developed on any considerable scale. Fixed nitrogen is now being pro-

duced by several well established methods, viz., the Haber, Birkeland-Eyde and cyanamide, and it does not seem that the use of titanium will be able to compete with these.

(15) PHOSPHORUS PENTOXIDE.

Another interesting invention is that of S. Peacock<sup>81</sup> involving the use of titanium dioxide as a means of liberating phosphorus pentoxide from bone ash or natural calcium phosphate. The residual calcium titanate could be used as a source of other titanium compounds. The reaction takes place at a high temperature, and the process is continuous, a special furnace having been designed for the purpose.



(16) APPLICATIONS IN PURE SCIENCE.

It is conceivable that titanium and its compounds might be employed in a variety of ways in purely scientific research. One such application deserves mention, and that is the use of pure titanium for the production of spectra in astronomical investigations.<sup>82</sup>

## PART II.

# THE DETECTION AND ESTIMATION OF TITANIUM IN ITS VARIOUS ASSOCIATIONS.

### Chapter V.

#### The Detection of Titanium in the Qualitative Analytical Course.

Titanium is so easily detected in the preliminary examination of any given material that its recognition in the systematic course of qualitative analysis is after all a secondary matter. The hydrogen peroxide test is one of great delicacy; and, since but few other substances undergo a like reaction, it is highly characteristic of titanium. Chromium, vanadium and molybdenum give blue, brownish red and yellow colors respectively (p. 61); but in case any of these are anticipated they can be removed by subjecting the original sample to a fusion with a mixture of sodium carbonate and sodium nitrate (20:3) and leaching the melt with hot water.<sup>1</sup> After dissolving the residue in sulfuric acid, the color test is made in the usual manner. Some idea as to the amount of titanium present may be formed by noting both the character and the intensity of the color, which will vary all the way from pale yellow to deep red-orange, depending upon the concentration of the solution with respect to titanium. Other and more delicate tests for titanium have been described in Chapter III (5).

An excellent scheme for the detection of those metals which when present in silicate minerals usually fail to yield satisfactory tests before the blowpipe is that of A. J. Moses and C. L. Parsons.<sup>2</sup> The volatile constituents are first expelled by roasting; whereupon the material is treated with hydrofluoric and sulfuric acids in a platinum dish with continued application of heat until the sulfuric acid has fumed freely for some time and it is reasonably certain that all hydrofluoric acid has been displaced.<sup>3</sup> Water is added and as much of the residue brought



into solution as possible. It is then filtered and the filtrate is divided into four approximately equal parts, which are tested in order for titanium, iron and aluminum, magnesium, and the alkalis; while the residue may be examined for the alkaline earths. Should the hydrogen peroxide reaction indicate that a considerable quantity of titanium is present, its amount can be better judged by making a phosphate precipitation according to G. S. Jamieson and R. Wrenshall,<sup>4</sup> which will be fully described under quantitative methods.

Another special scheme of qualitative analysis, which provides for the identification of chromium, nickel, cobalt, copper, titanium, zirconium, uranium, tungsten, molybdenum and vanadium in alloy steels, is that given by J. M. Camp.<sup>5</sup>

Titanium will be found in the "ammonium sulfide group",<sup>6</sup> provided a sufficient quantity of strong mineral acid be present to prevent its precipitation by hydrolysis during previous operations—a point not at all emphasized in most texts. Assuming the absence of the "silver group" (silver, mercurous mercury, lead and thallium in part) or its prior separation, A. A. Noyes and W. C. Bray<sup>7</sup> start with a volume of 40 cc., in which there is present 4 cc. of hydrochloric acid (sp. gr., 1.12) or 1.5 cc. of sulfuric acid (sp. gr., 1.84), and introduce hydrogen sulfide while the solution is kept near its boiling point—eventually saturating it with the gas at 70-90°C. In case molybdenum or the platinum metals are thought to be present, the test solution is cooled, after most of the sulfide has separated, saturated with hydrogen sulfide in the cold, closed up in a pressure bottle and heated for one hour in a bath of boiling water. In either event, the mixture is cooled, 60 cc. of water is added and the solution is again gassed with hydrogen sulfide till saturated. The reaction flask is then stoppered, shaken and allowed to stand for 15 minutes. After filtering and washing with hot water, a filtrate is obtained that is free from the "silver", "copper" and "tin" groups (with the possible exception of thallium).

The filtrate is made ammoniacal and hydrogen sulfide is passed in until the metals of the "aluminum" and "iron" groups have been completely precipitated.<sup>8</sup> The precipitate is washed with water containing a little colorless ammonium sulfide. It is then dissolved in hydrochloric acid (sp. gr., 1.12), and the hydrochloric acid is subsequently destroyed by repeated evaporations with nitric acid (sp. gr., 1.42). After filtering off any residual sulfur and evaporating to remove most of the surplus acid, the solution is made slightly alkaline with sodium hydroxide, sodium peroxide is added in the cold, followed by sodium carbonate, and the whole is boiled for 2 or 3 minutes. The filtrate contains the "aluminum" group and the precipitate consists of manganese, iron, cobalt, nickel, thallium, titanium, zirconium and a part

of the zinc originally present. It is dissolved in hydrochloric acid (sp. gr., 1.12), evaporated down and boiled with nitric acid till the hydrochloric acid has been decomposed; whereupon the manganese is precipitated with the aid of potassium chlorate. In the absence of phosphoric acid the iron, titanium, zirconium and thallium are precipitated by ammonium hydroxide—otherwise by the basic acetate process—being thus separated from nickel, cobalt and zinc. The hydroxides are dissolved in hydrochloric acid (sp. gr., 1.12) and the iron and thallium are extracted by shaking with ether and are recognized by appropriate tests. The ether is expelled from the aqueous solution by heating on the water bath and the hydrochloric acid is removed by evaporating with sulfuric acid to the fuming point of the latter. Hydrogen peroxide is added in some quantity, when the formation of an orange or yellow color indicates titanium. Sodium phosphate is next introduced, which gives rise to a white precipitate, if zirconium is present. In the filtrate from the zirconium phosphate, after bleaching out the color with sodium sulfite, the titanium comes down as phosphate, which enables the operator to judge of its amount. This analysis is shown in schematic form in Table V, and for further details the original article should be consulted.<sup>9</sup>

P. E. Browning, G. S. Simpson and L. E. Porter <sup>10</sup> have modified the analysis of the sub-group containing iron, thallium, titanium and zirconium in such a way as to avoid using the immiscible solvent principle. The hydroxides are dissolved in sulfuric acid. Hydrogen peroxide is added; whereupon the characteristic color of titanium will make its appearance. The solution is then made faintly alkaline with sodium hydroxide and sodium phosphate is added. The acid reaction is restored by means of a mixture of sulfuric acid and hydrogen peroxide, thus keeping the titanium peroxidized and dissolving all except zirconium phosphate. In the filtrate the iron and thallium are precipitated by sodium hydroxide, the hydroxides or phosphates dissolved with sulfuric acid and the solution treated with sodium sulfite and potassium iodide. In the filtrate from the thallic iodide, after boiling to remove sulfur dioxide, hydrogen peroxide is again added and the solution boiled to expell iodine and to oxidize the iron. The iron may now be detected by the thiocyanate test. The alkaline filtrate obtained above, which contains the titanium, is acidified with sulfuric acid and reduced by adding sodium sulfite, and perhaps an extra quantity of sodium phosphate may be needed to insure complete precipitation. Titanium, if present, comes down as white titanous phosphate.

Another scheme of qualitative analysis, in which the attempt is made to provide for the possible presence of nearly all the metallic elements, was published by Noyes <sup>11</sup> some years ago. Although titanium

TABLE V.\*  
ANALYSIS OF THE ALUMINUM AND IRON GROUPS FOR COMMON AND RARE ELEMENTS.  
To the solution add  $\text{NH}_4\text{OH}$  and pass in  $\text{H}_2\text{S}$ .

Ppt.		Filt.
Al, Cr, Be, Ti, Zr and V (partly) as hydroxides. Fe, Zn, Co, Ni, Mn, U and Tl as sulfides. Dissolve in $\text{HCl} + \text{HNO}_3$ , evaporate, add $\text{NaOH} + \text{Na}_2\text{O}_2 + \text{Na}_2\text{CO}_3$ .		
Ppt. (Fe Group)		Filt. (Al Group)
Mn, Fe, Co, Ni, Tl, Zr, Ti and Zn (partly) as hydroxides. Dissolve in $\text{HCl}$ , evaporate and heat with $\text{HNO}_3 + \text{KClO}_4$ .		Zn, Cr, Al, V, Be and U in solution as sodium salts. Add $\text{HNO}_3$ , dilute, add $\text{NaHCO}_3$ and heat in a closed bottle.
Ppt.	Filt. <sup>b</sup>	Ppt.
Mn	Add $\text{NH}_4\text{OH}$	Zn, Al and Be as hydroxides or carbonates.
Ppt.	Filt.	Neutralize with $\text{HNO}_3$ and add $\text{Pb}(\text{NO}_3)_2$ .
Fe, Ti, Zr and Tl	Co, Ni and Zn	
Dissolve in $\text{HCl}$ (sp. gr., 1.12) and shake with $(\text{C}_2\text{H}_5)_2\text{O}$ .		
Ether layer.		
Evaporate, dissolve in dilute $\text{H}_2\text{SO}_4$ , and add $\text{KI} + \text{Na}_2\text{SO}_3$ .		
Ppt.	Filt.	Ppt.
TiI (yellow).	Fe	$\text{PbCrO}_4$
Water layer.		Ppt.
Add $\text{H}_2\text{SO}_4$ , evaporate and add $\text{H}_2\text{O}_2 + \text{Na}_2\text{HPO}_4$ .		Pass in $\text{H}_2\text{S}$ .
Ppt.	Filt.	Filt.
Zr(OH)PO <sub>4</sub> (white).	Ti(SO <sub>4</sub> ) <sub>3</sub> (yellow).	PbS
Add $\text{Na}_2\text{SO}_3$		Add $\text{Br}_2$ , boil, neutralize and add $\text{HC}_2\text{H}_3\text{O}_2 + \text{Na}_2\text{HPO}_4$ .
Ppt.		Filt.
Ti(OH)PO <sub>4</sub> (white).		
		UO <sub>2</sub> NH <sub>4</sub> PO <sub>4</sub>
		Dissolve in $\text{HCl}$ , add $\text{NaCl} + \text{K}_2\text{Fe}(\text{CN})_6$ .
		Ppt.
		Add $\text{NH}_4\text{OH}$ with $\text{H}_2\text{S}$ . Red solution indicates V.
		(UO <sub>2</sub> ) <sub>2</sub> Fe(CN) <sub>6</sub> (reddish brown)

\* Scheme of Noyes, Bray and Spear: J. Am. Chem. Soc., 30, 481 (1908)—modified by Browning: Introduction to the Rarer Elements, 1912, p. 211. John Wiley & Sons.  
<sup>b</sup> Test for  $\text{H}_2\text{PO}_4$  and if present modify treatment.

and most of its associates were covered, these articles contained only a small part of the proposed work. In a recent paper by Noyes and Bray,<sup>12</sup> however, an outline of a plan is given for the systematic detection of the rarer chemical elements, and some rather radical changes in method have been made as compared with the earlier communication. The latter paper is complete in skeleton form, though many details remain to be added, and seems to be a decided improvement on the former in many respects. This work may prove directly useful in the examination of certain titaniferous materials. For example, minerals are known that contain the three "acid earths", tantalum, columbium and titanium, as well as other rare elements (see Chapter II, Table I).

## Chapter VI.

### Gravimetric Methods.

#### (1) THE ESTIMATION OF TITANIUM.

##### (a) Precipitation by Ammonium Hydroxide.

The solution of the titanic salt,<sup>1</sup> which may be the sulfate, chloride or nitrate, should contain a sufficient quantity of free mineral acid in the volume employed to prevent the precipitation of titanium on boiling. The precipitation is best performed in a platinum basin, but in lieu of this a beaker of borosilicate glass (e.g., "Pyrex") may be used. The solution, occupying a volume of 300-400 cc., is heated to the boiling point, the lamp removed just long enough for the liquid to become calm, and the titanium is thrown down by the gradual addition of pure ammonium hydroxide<sup>2</sup> in very slight excess. The liquid is heated and stirred for a few minutes in order to coagulate the precipitate; when it is allowed to stand until the titanic acid has subsided. The precipitate is collected on an ashless filter paper and thoroughly washed with a hot 2 per cent solution of ammonium nitrate. While still moist, the filter with its contents is placed in a tared platinum crucible, carefully dried, the paper smoked off, the residual carbon burned away and the crucible finally brought to constant weight over the Méker burner.

K. Bornemann and H. Schirmeister<sup>3</sup> have published the observation that, when determining titanium by precipitation with ammonium hydroxide, an error of loss may be incurred owing to the formation of titanium nitride—the presence of the nitride being indicated by a brownish color of the ignited residue. Although it has not been generally supposed that a nitride of titanium could be formed under these circumstances, C. Van Brunt<sup>4</sup> seems to have accepted the above statements in that he followed the precautions of Bornemann and Schirmeister (viz., evaporation of the unignited precipitate with sulfuric acid containing a little nitric acid) in setting the standard of his solution of titanic sulfate by ammonium hydroxide precipitation.

##### (b) Precipitation by Ammonium Phosphate.

There are several objections to the use of titanic phosphate as a gravimetric form. As obtained in analysis, it is of more or less indefinite

constitution, depending upon the precipitating conditions. V. Merz<sup>5</sup> obtained from hydrochloric acid solution a phosphate corresponding to the formula,  $Ti_2P_2O_6$ . F. A. Gooch,<sup>6</sup> however, while precipitating from a solution acidified with formic acid, found that the titanium phosphates so produced varied greatly in composition and in no case did one of them tally with the formula of Merz. Similar observations have been recorded by G. E. F. Lundell and H. B. Knowles.<sup>7</sup> Furthermore, the precipitate is difficult to filter and wash. In spite of these objections, it has been shown by E. J. Ericson<sup>8</sup> and still more conclusively by G. S. Jamieson and R. Wrenshall<sup>9</sup> that the phosphate of titanium which separates under accurately defined conditions may be used in exact analysis, if the weight of the ignited precipitate be multiplied by the empirical factor 0.336 to arrive at the weight of elementary titanium.<sup>10</sup> Jamieson and Wrenshall, in studying the process, found the instructions of Ericson to be somewhat imperfect—especially in so far as low results are obtained when small quantities (less than 0.007 gram) of titanium are under consideration, owing doubtless to a part of the titanic phosphate remaining in colloidal suspension. If, however, the acid concentration be kept small enough (3 cc. of hydrochloric acid (1:1) in 50 cc. of the solution), as little as 0.001 gram of titanium can be satisfactorily determined. But since these small precipitates require a long time to settle, and since too it is not practicable to filter very large amounts of the gelatinous phosphate, it is best to so regulate the size of the sample that not more than 0.030 gram nor less than 0.010 gram of titanium shall be present in any one experiment. The technique is as follows:

The solution, which may contain either sulfuric or hydrochloric acid, is first neutralized with ammonium hydroxide and then made acid again with 15 cc. of hydrochloric acid (1:1). The volume is made up to 100 cc. with water, and the solution is gassed with sulfur dioxide for 10 minutes.<sup>11</sup> After heating the solution to boiling, 20 cc. of a 10 per cent solution of ammonium phosphate is added; whereupon the titanium comes down as a white flocculent, somewhat gelatinous, precipitate. The boiling is continued for half an hour, and the precipitate allowed to settle for an hour or longer; when it is collected on asbestos in the perforated crucible, using moderate suction and not allowing the crucible to drain completely until thorough washing has been effected with hot water. The precipitate is carefully dried, ignited for 15 minutes at the highest temperature of a good Bunsen burner, cooled and weighed. On multiplying the value so obtained by 0.336, the product will be the weight of the titanium.

(c) Precipitation by the Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron")

Under the name "cupferron", O. Baudisch<sup>12</sup> introduced into analytical chemistry the ammonium salt of nitrosophenylhydroxylamine as a precipitant for either copper or iron and indirectly for the separation of these two metals from each other. Since then, this remarkable reagent has received a good deal of attention on the part of various chemists. About forty articles dealing with the subject in one way or another have already appeared in scientific journals,<sup>13</sup> and many useful separations have been worked out with gratifying results, some of which had previously confronted the analyst with much difficulty (cf. pp. 58-9).

In connection with other work, K. Schröder<sup>14</sup> suggested the possibility of precipitating either titanium or zirconium with cupferron; but gave no experimental data. It was not long, however, before I. Bellucci and L. Grassi<sup>15</sup> fully demonstrated that the precipitation of titanium by cupferron is not only feasible but that highly accurate results can be obtained in this way. Our knowledge of suitable precipitating conditions has been extended—partly by the author<sup>16</sup> and partly by Lundell and Knowles.<sup>17</sup>

The titanium solution may contain almost any acid, including sulfuric, hydrochloric, nitric, acetic, tartaric, citric, etc. Nitric acid in high concentration is not permissible because of its oxidizing action on the nitrosophenylhydroxylamine. If sulfuric acid be the acidifying agent, as is usually the case, it may make up as much as 40 per cent by volume of the entire solution without exerting any solvent action on the precipitate;<sup>18</sup> though such large amounts of acid have not been found necessary in any of the actual separations (to be described later).

The test solution, containing about 40 cc. of sulfuric acid (1:1), is diluted with water to a volume of 400 cc. It is not well to attempt the precipitation of more than 0.2 gram of titanic oxide at one time, and even this will require a 15 cm. filter. The beaker is placed in a bath of cracked ice, and a recently filtered 4 per cent solution of cupferron is added drop by drop with constant stirring till present in considerable excess. One and a half times the theoretical amount will do no harm. The titanium comes down as a canary yellow flocculent precipitate, which is easily coagulated by stirring and filters rapidly without the aid of suction. The supernatant liquid should be tested by adding a little more of the reagent. The formation of a small white precipitate of nitrosophenylhydroxylamine, which soon vanishes, indicates that the reagent has been added in excess, while a yellow turbidity shows that more is needed. It is well also to test the filtrate. The precipitate is collected on a paper filter,<sup>19</sup> set in a long stem funnel and braced by a

perforated platinum cone, and is washed twenty times with ice-cold hydrochloric acid (1:9). After having been sucked free from drainage liquid at the pump, the paper and precipitate are placed in a tared platinum crucible and dried in the oven at 110°C. The ignition is begun with a very small flame. After the first violent gush of smoke, the temperature is raised gradually until the carbon has been consumed, and then the full power of the Méker burner is applied for 20 minutes. The product is titanic oxide of definite composition.

#### (d) Precipitation by Hydrolysis of the Sulfate.

The precipitation of titanium by prolonged boiling of a nearly neutral and highly diluted solution of the sulfate is perhaps the oldest method for separating the element from its common associates and subsequently estimating it as the dioxide. In view of its many disadvantages the process may now be considered practically obsolete.<sup>20</sup> When titanic acid separates from solution by a very slow process of hydrolysis, it is apt to adhere to the surface of a glass vessel so tenaciously as to make complete removal well nigh impossible. Moreover, some solvent action on the glass and consequent contamination of the precipitate is inevitable during the long period of boiling, the use of a platinum receptacle being precluded by the large volume usually recommended—more than 3 liters, according to W. Bettel.<sup>21</sup>

The hydrolysis will go to completion when the solution contains 0.5 gram of sulfuric acid for every 100 cc. and the boiling is kept up for 6 hours with renewal of the evaporating water from time to time.<sup>22</sup> A little sulfuric acid should be added to the wash water.

#### (e) Precipitation by Hydrolysis of the Chloride.

The precipitation of titanium by boiling a slightly acid chloride solution (free from sulfates), containing also sulfurous acid, with the object of separating it from iron and other metals, is generally attributed to C. Baskerville;<sup>23</sup> though the same principle seems to have been employed by P. Berthier<sup>24</sup> at a much earlier date.

If the solution contain sulfuric acid, it is treated with ammonium hydroxide in excess *without boiling*, filtered and the precipitate washed twice with hot water. The filtrate is rejected. The precipitate is dissolved in dilute hydrochloric acid. After nearly neutralizing with ammonium hydroxide or ammonium carbonate, the solution is diluted to 300 cc., saturated with sulfur dioxide and boiled until the titanic acid has separated out and the odor of sulfur dioxide is faint. The wash water should contain a little sulfurous acid; otherwise the determination is completed in the usual manner.



(f) Precipitation by Hydrolysis in the Presence of an Alkali Acetate.

The hydrolysis of titanic acetate forms the basis of the well known method of Gooch<sup>25</sup> for separating titanium and aluminum. Two slightly different procedures were employed by him, either of which is known to yield a satisfactory result.

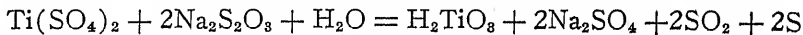
The solution, containing free sulfuric acid and a small quantity of alkali sulfate perhaps, is treated with ammonium hydroxide until it smells faintly of that reagent. Acetic acid is then added in distinct excess. The titanium is quantitatively precipitated on boiling.

The following technique, which is very similar to the second *modus operandi* of Gooch, has been used by the author<sup>26</sup> in standardizing solutions of titanic sulfate,<sup>27</sup> and has been found to be very reliable:

The solution is made nearly neutral with ammonium hydroxide—the stopping point being indicated by the appearance of a faint permanent turbidity. One cubic centimeter of a strong solution of ammonium bisulfite is added, followed by 15 grams of ammonium acetate and 20 grams of glacial acetic acid, and the volume is made up to 400 cc. with water. The solution is brought rapidly to boiling and maintained in ebullition for 1 minute. The precipitate is collected on a filter paper and washed twenty times—first with boiling 5 per cent acetic acid and finally with hot water. It is ignited to titanic oxide in the ordinary way—constant weight being attained on heating for 20 minutes over the Méker burner.

(g) Precipitation by Hydrolysis in the Presence of Sodium Thiosulfate.

A. Stromeayer<sup>28</sup> has applied G. Chancel's<sup>29</sup> thiosulfate method to the separation of titanium and zirconium from iron. This compound exerts the necessary buffer action for hydrolyzing the titanium salt and at the same time reduces the iron to the ferrous condition by reason of the sulfurous acid formed as a product of its decomposition.



On the other hand, a fixed alkali is introduced, which may be occluded in the titanic acid precipitate to some extent, and the filtrate is rendered milky by the passage of finely divided sulfur through the paper.

The sulfate solution is nearly neutralized with sodium carbonate, treated with an excess of sodium thiosulfate, diluted to 400-500 cc. and boiled for some time.

(h) Precipitation by Hydrolysis in the Presence of Phenylhydrazine or Aniline.

The use of phenylhydrazine as a precipitant for aluminum was first proposed by W. H. Hess and E. D. Campbell.<sup>30</sup> They showed that aluminum (along with phosphoric acid) could be separated from iron, manganese, calcium and magnesium by adding the phenylhydrazine to a solution of these substances previously deoxidized by sulfurous acid. E. T. Allen<sup>31</sup> has studied the action of organic bases in general and of phenylhydrazine and aniline in particular, and has succeeded in extending the work of Hess and Campbell to include a greater number of inorganic bodies and in more accurately defining the conditions under which good separations may be expected. Allen has found that in a similar manner titanium is precipitated free from iron, but that the permissible acidity with titanium is considerably greater than with aluminum. Aniline precipitates titanium also; but phenylhydrazine is preferable, especially when iron is present, since it exerts a reducing action. As applied in rock analysis to the separation of aluminum, phosphorus, titanium and zirconium from iron, manganese, calcium and magnesium the method is as follows:<sup>32</sup>

The chloride solution, amounting in volume to 100-200 cc. according to the quantity of aluminum, etc. expected, is heated and the iron fully reduced by adding from 5 to 20 drops of a saturated solution of ammonium bisulfite. If a deep red color appears due to the formation of ferric sulfite, it means that the acid concentration is too low; hence a few drops of hydrochloric acid should be added. The solution is quickly neutralized with ammonium hydroxide, and then made acid again with several drops of dilute hydrochloric acid. If the last operation is performed too slowly, a little ferric hydroxide is formed by atmospheric oxidation and may not dissolve readily in the acid. From 1 to 3 cc. of freshly distilled phenylhydrazine is now introduced into the still hot solution, and, after clotting the precipitate by stirring, the beaker is set aside (for not more than an hour) to permit settling. A brown precipitate need cause no concern; since the color is due to organic matter and not to iron. The precipitate is washed with a warm dilute solution of phenylhydrazine bisulfite,<sup>33</sup> and ignited in the customary manner. As Allen<sup>34</sup> states, a double precipitation will probably be needed to free titanium entirely from iron when much of the latter is present.

When titanium alone is to be determined, the addition of ammonium bisulfite is doubtless unnecessary. The neutral solution is treated with a half dozen drops of hydrochloric acid (1:1); otherwise the operations are as given above.

## (2) THE SEPARATION OF TITANIUM FROM THE ALKALIS.

Any of the processes described in (1) might be used for separating titanium from the alkali metals, excepting (g) when the alkalis are to be estimated in the filtrate.

It is of great importance, however, to bear in mind the ever present phenomenon displayed by precipitates like titanitic acid, which have a marked tendency to return to the colloidal condition, of including in their interstices otherwise soluble matter, which is removed in the course of washing only with great difficulty or not at all.

In this connection Gooch<sup>35</sup> has pointed out that, in precipitating titanium from solutions of titanitic sulfate containing also some sodium or potassium sulfate, higher results are obtained by treating with ammonium hydroxide in excess and then boiling than by first neutralizing with ammonium hydroxide, adding acetic acid just in excess and boiling. In other words, the occlusion is greater from an alkaline than from an acid medium.<sup>36</sup> Nevertheless, two precipitations by ammonium hydroxide will surely suffice to liberate titanium from relatively large amounts of alkali salt.

The first precipitation should be made in the cold and the precipitate washed only a few times with cold water. As much of the titanitic acid as possible is returned to the original vessel by means of a small platinum spatula, and that remaining is dissolved by running hot dilute hydrochloric acid (1:3) through the filter and back into the beaker or dish in such a way as to completely wash down the sides of the container as well as the stirring rod and spatula. The second precipitation is made at or near the boiling temperature in a volume of about 200 cc., the ammonium hydroxide being added carefully from a burette in sufficient quantity to produce complete hydrolysis but not beyond the turning point of methyl red ( $p^H$ , 4.4 to 6.0). The washing should be very thorough (about twenty times); using a hot 2 per cent solution of ammonium chloride. If one has a sulfate solution to start with instead of a chloride solution, it would be best to introduce no other negative radical in case the alkali salt is to be recovered from the filtrate by evaporation and ignition; hence the first precipitate should be dissolved in sulfuric acid and ammonium sulfate added to the wash water.

The amount of alkali carried down under varying conditions and held by the titanitic derivative of nitrosophenyldiethylamine in a way not removed by thorough washing is not as well known as would be desired. Some experiments by E. M. Hayden, Jr. and the author<sup>37</sup> on zirconium showed that from solutions containing rather large amounts of potassium sulfate<sup>38</sup> the zirconium precipitates produced by cupferron undergo a noticeable though not excessive increase in weight.

Because of the great similarity in the behavior of titanium and zirconium toward that cupferron reagent, it seems reasonable to suppose that inclusions of like magnitude would occur in the case of titanium also. In fact, Lundell and Knowles<sup>39</sup> have found by actual test that this is so. Although the error from this cause cannot be very serious under ordinary working conditions, the following procedure will in any event remedy the trouble:

The first precipitation is made by ammonium hydroxide in the cold. After redissolution in hot dilute sulfuric acid (1:5), using 120 cc. in all, the titanium is determined with the aid of cupferron exactly as described in (1) (c).

The organic matter in the filtrate may be destroyed by nitric acid,<sup>40</sup> and the analysis for alkalis made by well known processes.

### (3) THE SEPARATION OF TITANIUM FROM THE ALKALINE EARTHS (MAGNESIUM).

No special difficulty is encountered in separating titanium from the alkaline earths. It is obviously necessary to avoid the presence of sulfuric acid or sulfates in dealing with calcium, barium or strontium. This remark does not of course apply to magnesium nor to calcium in traces.<sup>41</sup>

Two precipitations by ammonium hydroxide (free from ammonium carbonate) are sufficient to give a titanic acid free from members of this group.

Cupferron does not precipitate the alkaline earths, as R. Fresenius<sup>42</sup> has shown; neither does phenylhydrazine.<sup>43</sup>

No doubt this separation could be effected by precipitation with ammonium phosphate, or by hydrolysis of titanic chloride or acetate.

If it is desired to recover the alkaline-earth metals from the filtrate, in which case it is perhaps best to use the simple ammonium hydroxide precipitation, since it introduces no interfering substance, it is done in accordance with familiar processes.

### (4) THE SEPARATION OF TITANIUM FROM THE OTHER MEMBERS OF THE ALUMINUM AND IRON GROUPS.

#### (a) Titanium from Iron.

#### (\*) The Sulfide Process in its Various Modifications.

It has long been known that certain metallic elements, which normally form insoluble hydroxides, carbonates, phosphates, etc., with appropriate reagents, fail to do so when certain organic substances, e.g., citric acid, tartaric acid, dextrin, sucrose, glucose, lactose, etc. . . . ,

are present in sufficient quantity. Moreover, the inorganic compound sodium pyrophosphate, strangely enough, is capable of performing the same function. This "holding power" has been studied by L. J. Curtman and H. Dubin<sup>44</sup> with respect to iron, chromium and aluminum. Referring to the above list, in which the substances are arranged in descending order as to holding power, they find citric acid to be the strongest and lactose the weakest and that the four carbohydrates possess this property but feebly as compared with the two acids. It is also interesting to note that mandelic acid, which contains a benzene nucleus, has very little power to prevent the precipitation of titanium by ammonium hydroxide.<sup>45</sup> Confining our attention then to the organic acids, we may generalize by saying that this property, whatever its mechanism may be, is closely connected with the hydroxyl group; since it is exhibited by glycollic and not by acetic acid—two acids related to each other by the substitution of one hydroxyl group for a hydrogen atom. Notwithstanding the existence of a complex compound containing the metal, which prevents it from undergoing many of its ordinary reactions, it is in some cases possible to bring about complete precipitation by means of certain reagents, notably, hydrogen sulfide, ammonium salt of nitrosophenylhydroxylamine, ammonium phosphate in the case of titanium<sup>46</sup> and reducing sugars in the presence of alkali hydroxide (Fehling's test).

Many years ago H. Rose<sup>47</sup> separated titanium from iron by precipitating the latter as sulfide from an ammoniacal solution containing ammonium tartrate, and recovered the titanium from the filtrate by evaporating to dryness and destroying the organic acid by ignition. Even now, the sulfide process is one of the best methods that we know for the separation of these two elements; but the subsequent operations of Rose, viz., evaporating the solution and burning off the organic matter, must be regarded as eminently inconvenient.

The oxidation of the tartaric acid by potassium permanganate, as proposed by Gooch,<sup>48</sup> presents great advantages as compared with the older ignition method, and until quite recently it was an operation to which the analyst frequently had recourse. The objection to potassium permanganate, in that another metal is introduced into the analysis, which may be subsequently co-precipitated with the titanium in some measure, was overcome, first by H. Wdowiszewski<sup>49</sup> and later by the author,<sup>50</sup> by using nitric acid. A still better expedient than any of the above is to precipitate the titanium with the cupferron reagent, which acts independently of organic hydroxyacids—thus rendering their oxidation unnecessary.

To the solution, which should be of small bulk, preferably not much greater than 100 cc., tartaric acid is added in amount equal to three

times the aggregate weight of the oxides to be held by it in solution.<sup>51</sup> To facilitate the reduction of the iron the solution is made neutral with ammonium hydroxide and then acid again with 2.5 cc. of sulfuric acid (1:1). Hydrogen sulfide is then introduced until the solution has become colorless. Unless the iron is thus deoxidized before precipitation, titanium will be in part thrown down also.<sup>52</sup> Ammonium hydroxide is then added in decided excess and more hydrogen sulfide passed in until the iron has been completely precipitated as ferrous sulfide. The iron sulfide is filtered off, using a paper of close texture, and washed ten times with a fresh solution of ammonium sulfide (made by passing hydrogen sulfide into water containing about 25 cc. of ammonia (sp. gr., 0.92) in a liter).

*Optional Procedure No. 1.* The filtrate, which should be pale yellow and perfectly clear, is strongly acidified with sulfuric acid and the hydrogen sulfide thus liberated expelled by boiling. A strong solution of potassium permanganate (made by dissolving two and one-half times the weight of the tartaric acid used of permanganate crystals in a little water) is added gradually to the hot solution; whereupon vigorous action ensues with formation of brown hydrated manganese peroxide in the latter stages. When the brown precipitate does not perceptibly dissolve in the boiling solution, one may be sure that the tartaric acid has been oxidized as far as formic acid, which is all that is required in the present case; but for greater certainty it is well to continue adding the permanganate until its color has been imparted to the entire solution. After clearing the liquid by means of a small quantity of ammonium bisulfite, ammonium hydroxide is added to the cold solution in slight excess, followed at once by acetic acid in considerable excess, and the titanium precipitated by boiling for a few minutes. The precipitate is washed with water containing both sulfurous and acetic acids and ignited as usual in a platinum crucible. Since this precipitate is generally not quite pure, it is fused with 1 gram of dry sodium carbonate, treated in the crucible with 2.5 cc. of sulfuric acid (sp. gr., 1.84)—allowing the action to proceed spontaneously as far as it will and then warming the covered crucible very cautiously, the syrupy solution poured into 100 cc. of cold water and the titanium thrown down again. To this end, ammonium hydroxide is added in sufficient quantity to just precipitate the titanium, and the titanous acid is dissolved by adding enough sulfuric acid of known strength (corresponding to 2.5 grams of pure acid), acetic acid is introduced so as to make up from 7 to 11 per cent of the final volume in absolute acid and finally 20 grams of sodium acetate is stirred in. The solution, which should occupy a volume of about 400 cc., is brought rapidly to boiling and the ebullition continued for only one minute.

The precipitate is washed first with acetic acid of 7 per cent strength and then with hot water, and ignited over the Bunsen burner to constant weight.

*Optional Procedure No. 2.* The filtrate from the ferrous sulfide is acidulated with 15 cc. of sulfuric acid (sp. gr., 1.84), the hydrogen sulfide boiled out, the solution transferred to a large basin (preferably of platinum) and reduced to small volume by the moderate application of heat. The concentrated solution is then transferred to a deep form platinum dish of about 250 cc. capacity, evaporated further to incipient charring of the tartaric acid and then, after covering the dish with a watch glass, the heating is continued until charring and frothing have occurred as much as the capacity of the vessel will permit. After cooling a little, 5 cc. or more of *fuming* nitric acid is introduced through the lip opening with a bulbed pipette. A vigorous reaction takes place accompanied by much effervescence and copious evolution of brown fumes. The organic matter gradually disappears. The effervescence becomes steady, finally ceases and the sulfuric acid begins to fume. The pale yellow syrupy liquid is poured into 100 cc. of cold water, filtered from extraneous matter if necessary and the titanium precipitated by hydrolysis of the acetate, as described under (1) (f).

*Optional Procedure No. 3.* After acidifying the filtrate with 40 cc. of sulfuric acid (1:1) and boiling out the hydrogen sulfide, the titanium is precipitated by cupferron exactly as described in (1) (c).

In the author's opinion it is best to reject the iron sulfide precipitate and determine the iron volumetrically in another aliquot part of the original solution.<sup>53</sup> If, however, it is desired to make a gravimetric determination of the iron, the washed sulfide may be advantageously used for this purpose. In the absence of other metals that form insoluble sulfides, the precipitate might be weighed as the sulfide ( $\text{FeS}$ ) in accordance with the method of Rose;<sup>54</sup> but it is doubtless better in any case to dissolve in acid, oxidize the iron, reprecipitate with ammonium hydroxide, and weigh as ferric oxide.

If the precipitate is large in amount, it is removed from the filter with a platinum spatula as far as possible. Hot hydrochloric acid (1:1) is then run through the paper and the solution is caught in the original beaker. From 20 cc. to 50 cc. of the acid may be employed, depending upon the quantity of the precipitate and the size of the filter, and the paper is thoroughly washed with hot water. Five cubic centimeters of nitric acid (1:1) is then added and the solution boiled to oxidize the iron. Ammonium hydroxide is now added in not too great excess, the ferric hydroxide collected on the same paper, washed with hot 2 per cent ammonium nitrate solution and ignited apart from its filter by the method of R. W. E. Bunsen.<sup>55</sup>

**(\*\*) The Peroxide-Alkali Process.**

The fact that a peroxidized solution of titanium does not yield an immediate precipitate with an alkali hydroxide (p. 57) was first utilized by A. Classen<sup>56</sup> for the separation of titanium and iron. P. H. Walker,<sup>57</sup> in testing the matter with 0.1 gram each of ferric and titanous oxides, found that three precipitations were necessary under the conditions of his experiment to free the ferric hydroxide entirely from titanium. Bornemann and Schirmeister,<sup>58</sup> on the other hand, report satisfactory results when the method is carried out as follows:

To the cold acid solution containing a considerable excess of hydrogen peroxide ("perhydrol") enough potassium hydroxide is added to completely precipitate the iron. The ferric hydroxide is washed with cold water containing a little peroxide. The filtrate is treated with sulfur dioxide to destroy the peroxide and the titanium is precipitated twice with ammonium hydroxide. The method is said to be especially applicable to the estimation of small amounts of titanium in company with much iron.

**(\*\*\*) The Electrolytic Process.**

The electrolytic deposition of iron in the metallic state as a means of separating it from titanium has been recommended by several investigators; but the proper working conditions do not seem to have been as definitely laid down as would be desired. In general, two courses have been followed: first, the iron is deposited on a platinum cathode from a complex electrolyte (oxalate, lactate, tartrate, citrate, etc.) and, second, within a mercury cathode from a sulfate solution of small volume slightly acidified with sulfuric acid.

R. K. Murphy<sup>59</sup> has investigated the former type of method. He finds that from a solution containing ammonium oxalate the separation is not satisfactory. Better results, however, may be obtained by using a citrate electrolyte, provided the amount of titanium relative to the iron be not too great. The conditions, finally adopted by Murphy as being the best, are as follows:

The solution of the sulfates is made just neutral with ammonium hydroxide and then acid again with a few drops of dilute sulfuric acid. Sodium citrate solution (equivalent to 1.8 grams) is added, followed by a little citric acid (0.059 gram), and the solution thoroughly stirred. The clear yellow-brown liquid is then heated to boiling, transferred to a platinum dish (Classen's form), diluted to about 200 cc. and electrolyzed over night with a current of  $ND_{100} = 0.55$  amp. and 2.8 volts at a temperature of about 30°C. The deposit is described as being uniform and adherent. The titanium is determined by reduction with zinc and hydrochloric acid and titration with methylene blue<sup>60</sup> (p. 147).



Murphy's test analyses are very good; but the maximum quantity of titanium experimented with was 0.0125 gram in admixture with 0.1543 gram of iron. The values for iron obtained by weighing the deposit are slightly in excess of the correct amount, due no doubt to occlusions of carbon; but the error is not intolerable.

E. F. Smith <sup>61</sup> has obtained satisfactory results in trial experiments on the separation of iron from titanium when 0.1 gram of each metal was present.

A beaker of 50 cc. capacity with sealed-in platinum wire near the bottom and containing enough mercury to serve as cathode is tared before the experiment. The solution is acidified with 0.25 cc. of sulfuric acid (50 per cent) and electrolyzed with a current of not over 5 volts for 5 hours at the ordinary temperature. The mercury is washed with water without interrupting the current, then with absolute alcohol and finally with ether. When the odor of ether is no longer perceptible, the beaker is wiped on the outside and placed in a desiccator over sulfuric acid for 15 minutes. It is then ready for weighting.

The very small volumes employed by Smith <sup>62</sup> in connection with the mercury cathode and rotating anode do not seem practicable in the analysis of titaniferous materials; hence the technique will not be given here.

G. Magri and G. Ercolini <sup>63</sup> employ a membrane of parchment paper in the electrolytic separation of iron from titanium and aluminum; but the advantage to be gained by using a membrane is not apparent; since they evaporate both the anodic and cathodic solutions in order to recover the titanium and aluminum.

#### (\*\*\*\*) The Ether Process.

The separation of iron from various other elements by shaking the solution of the chlorides in hydrochloric acid of specified strength with ether was first brought out by J. W. Rothe.<sup>64</sup> Since then this principle has been frequently applied in analysis, and has been found especially useful when the object is to remove a very large amount of iron (as in iron and steel analysis) from relatively small amounts of certain other constituents. Titanic chloride, along with most other metallic chlorides,<sup>65</sup> is practically insoluble in ether under the conditions of experiment; hence it may be assumed to remain entirely in the aqueous layer. On the contrary, ferric chloride <sup>66</sup> is very much more soluble in ether than in aqueous hydrochloric acid,<sup>67</sup> and the iron distributes itself between the two layers in accordance with the partition law:

$$100.s. + c_1/c_2 = k$$

Hence, by repeating the shaking process several times the iron is separated almost entirely from the titanium.

O. L. Barnebey and R. M. Isham,<sup>68</sup> who have applied the ether extraction to the analysis of rutile and highly titaniferous iron ores with great success, give the following procedure:

The solution of the chlorides, obtained by dissolving the mixture of sodium titanate and ferric oxide<sup>69</sup> in hydrochloric acid (sp. gr., 1.11), is concentrated by evaporation to a volume of 15-20 cc., and after cooling 2 cc. of hydrochloric acid (sp. gr., 1.18) is added; whereupon the whole is transferred to a separatory funnel, the original vessel being rinsed with small portions of hydrochloric acid (sp. gr., 1.11).

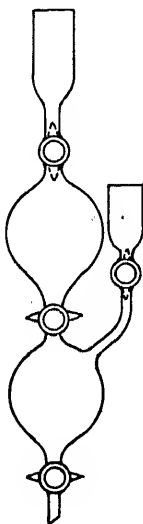


FIG. 13.—J. W. Rothe's shaking funnel.

An equal volume of ether, previously saturated with hydrochloric acid (sp. gr., 1.18) by thorough shaking, is added to the solution. The top opening of the funnel is closed with a solid rubber stopper, and with the stop-cock open the inverted funnel is vigorously shaken. After allowing 10 minutes for settling, the aqueous layer is drawn off into another separatory funnel. The ether is washed twice by shaking with 5-10 cc. portions of hydrochloric acid (sp. gr., 1.11), and these rinsings are added to the aqueous solution. The ethereal solution may now be rejected. These operations are repeated in order until the ether layer no longer assumes a greenish color, showing that iron has been completely removed (or as nearly so as possible under the working conditions). Three or four treatments will usually suffice. The ether is expelled by warming on the water bath, 20 cc. of sulfuric acid (1:1)

is added and, changing to the hot plate, the evaporation is continued until fumes of sulfur trioxide make their appearance. The well cooled solution is diluted to about 100 cc. (any platinum present may be removed at this point) and nearly neutralized with ammonium hydroxide. Ammonium bisulfite (equal to 1 or 2 grams of the salt) is added, and the solution is warmed on the hot plate for half an hour. Ten to 15 grams of ammonium acetate is added and 5-10 cc. of glacial acetic acid, and the solution is boiled until the titanous acid has precipitated. The remaining operations have already been described (pp. 92 and 97).

Instead of using two separatory funnels the Rothe funnel (Figure 13), fully described by O. Bauer and E. Deiss,<sup>70</sup> may be advantageously employed.

#### (\*\*\*\*\*) High Temperature Processes.

F. Bourion<sup>71</sup> has succeeded in separating iron from titanium by passing a current of dry hydrochloric acid gas, in which some sulfur monochloride has been entrained, over a heated mixture of ferric and titanous oxides. This is but a modification of the method previously suggested by C. Friedel and J. Guérin,<sup>72</sup> sulfur monochloride being substituted for chlorine. Volatile ferric chloride is formed while the titanium dioxide is not attacked.

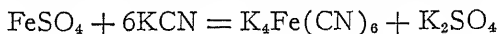
The correct proportion of the chloride of sulfur is secured by placing it in an ice bath and passing the dry hydrochloric acid gas over it. The operation is started at 200°C. and the temperature is finally brought up to 700-750°C. The time required for the experiment varies from 2½ to 4 hours.

Gooch and Havens<sup>73</sup> have established conditions whereby an excellent separation of iron from aluminum may be accomplished. A suitable mixture of hydrochloric acid and chlorine is prepared by dropping sulfuric acid into a flask containing concentrated aqueous hydrochloric acid, sodium chloride and a little manganese dioxide. The porcelain boat containing the mixed oxides is placed in a wide combustion tube. The gas stream enters at one end of the tube and passes out at the other through a water trap. Meanwhile the desired temperature, from 200°C. to 300°C., is maintained by means of a small furnace. The time required for the process varies somewhat with the condition of the oxide to be volatilized and the prevailing temperature; but an hour's heating will usually suffice for the removal of 0.1 gram of iron, even though the temperature of 200°C. be not exceeded. By heating the tube hotter the time may be shortened; but, to avoid mechanical loss, it is better to employ the lower temperature until near the end of the operation, when the heat may be increased for a few minutes so as to insure the expulsion of the last trace of ferric chloride. In like manner,

F. S. Havens and A. F. Way <sup>74</sup> have obtained very satisfactory separations of iron from beryllium, chromium and zirconium. No doubt the same technique would apply equally well to iron and titanium.

(\*\*\*\*\*) **The Cyanide-Ammonia Process.**

Bornemann and Schirmeister <sup>75</sup> have brought out an ingenious method for separating titanium from iron, which depends upon treating the slightly acidified and fully deoxidized solution with ammoniacal potassium cyanide. The iron remains in solution, presumably as potassium ferrocyanide, while the titanium precipitates as titanous acid.



From 0.3 to 0.5 gram of the substance is dissolved (e.g., by a pyrosulfate fusion), and the solution, which must not be too acid, is made up to a volume of 500-600 cc. From 20 to 30 cc. of a concentrated solution of sodium bisulfite is then added, and the liquid is warmed gently (at about 50°C.) until the iron has been completely reduced to the ferrous condition (thiocyanate test). While maintaining a temperature of 40°C., 70-100 cc. of a solution of potassium cyanide in concentrated ammonia is added promptly with vigorous stirring. The total amount of cyanide added should be from seven to eight times the weight of the sample, and with materials very low in iron this may be greatly reduced. The solution is heated to boiling until the precipitate becomes pure white and the supernatant liquid acquires a yellowish-green color. The time of heating, however, should not be greater than about 10 minutes. When cold, the solution is filtered as quickly as possible, and the precipitate is washed first with an ammoniacal ammonium sulfite solution and then with hot water. The precipitate, as it may contain alkali, is dissolved while still moist in hot dilute hydrochloric acid and reprecipitated with ammonium hydroxide. The dried precipitate is removed from its filter as far as possible, treated in the crucible with a few drops of sulfuric acid containing some nitric acid, the acids evaporated off, the ash of the paper added and the whole brought to constant weight by strong ignition (cf. p. 88).

The iron may be recovered from the filtrate, if so desired; but it is perhaps better to determine it in a separate portion of the material (see the original article).

(\*\*\*\*\*) **The Phosphate Process.**

Titanium can be separated from iron by precipitating the former as the phosphate in the manner already given under (1) (b). Jamieson and Wrenshall, <sup>76</sup> however, have shown that the iron can be more rapidly

reduced than by sulfurous acid, if hydrogen sulfide be applied in the following way:

The solution is treated with 2 grams of tartaric acid and enough ammonium hydroxide is added to render it slightly alkaline. Hydrogen sulfide is then passed in until the iron has been completely precipitated as ferrous sulfide. Fifteen cc. of hydrochloric acid (1:1) is then added, and the solution is warmed until the iron sulfide has entirely redissolved. Twenty cc. of a 10 per cent solution of ammonium phosphate is added to the liquid, which should occupy a volume of 100 cc. and be maintained at the boiling temperature; otherwise the procedure is identical with that given above.

(\*\*\*) **Hydrolytic Processes.**

The hydrolysis of titanic sulfate in the presence of sulfurous acid as a means of separating titanium from iron may be dismissed on account of those inconveniences attending its application that have already been mentioned in (1) (d).

The precipitation of titanic acid by boiling a nearly neutral solution of titanium chloride containing sulfurous acid, commonly known as Baskerville's <sup>77</sup> method, offers distinct advantages as compared with the sulfate hydrolysis in that the hydrolytic decomposition takes place quickly in a small volume of solution and the precipitate formed is readily handled. Baskerville himself records only two test analyses, which were made on a pure titanium salt; though he states without qualification that the separation from iron is quantitative in one operation and that aluminum also remains in solution. Some difference of opinion has been expressed, however, as to the nicety with which this process is capable of parting titanium from iron. Thus, W. F. Hillebrand <sup>78</sup> says that, in applying the method to the analysis of titaniferous iron ores, the precipitates were found to contain noteworthy amounts of iron. In the light of further experience, however, this statement has been withdrawn and replaced by a much more favorable comment.<sup>79</sup> V. Lenher and W. G. Crawford <sup>80</sup> speak of the method as giving uniformly excellent results. Murphy,<sup>81</sup> who seems to have studied this method with a good deal of care, claims that a successful separation depends upon the acidity of the test solution and that, after some practice, one may adjust this so as to obtain a titanic acid precipitate entirely free from iron. He suggests further that the filtrate be tested for completeness of precipitation by again saturating with sulfur dioxide and boiling. Moreover, L. E. Barton <sup>82</sup> emphasizes the difficulty in deciding on the proper degree of acidity when analyzing materials very low in iron (such as titanium pigments). He therefore recommends that enough ferric salt be intentionally added to impart color to the precipitate which forms momen-

tarily while the solution is being neutralized with ammonium hydroxide. Barton's directions, which are more definite than those usually given, are as follows:

The chloride solution, scrupulously free from sulfates and occupying a volume less than 150 cc., is maintained at a temperature of about 50°C. and ammonium hydroxide added gradually with stirring until the precipitate which first forms just redissolves. The neutralization is continued by adding the reagent dropwise until a slight permanent precipitate is produced, which is redissolved in the least possible amount of dilute hydrochloric acid; thereupon 2 cc. of hydrochloric acid (1:1) is added. The solution is then diluted to 400 cc., thoroughly gassed with sulfur dioxide and boiled until it smells only faintly of sulfurous acid. The liquid is filtered while still hot through a filter paper, washed with hot water (or perhaps better water containing sulfurous acid) and finally calcined for half an hour at not less than 900°C.

Several chemists,<sup>83</sup> in order to save time, have modified the Gooch<sup>84</sup> method by omitting the sulfide precipitation of the iron and hydrolyzing titanic acetate in the presence of sulfurous acid.<sup>85</sup> The titanic acid so obtained is seldom entirely free from iron and must therefore be redissolved and reprecipitated in the manner already described (p. 97).<sup>86</sup> This makes no difference with materials high in aluminum, since the first titanium precipitate is never free from that ingredient (see (4) (b)); but in the case of non-aluminous substances—or those containing only a very little aluminum—it is quite possible, after removing the iron as sulfide, to obtain a pure titanic acid in one precipitation; provided, of course, that phosphoric acid is absent.<sup>87</sup> Further details will be given under the analysis of titanium minerals.

Titanium may be separated from iron by boiling a slightly acid solution containing sodium thiosulphate as described under (1) (g). If much iron is present, it contaminates the precipitate to some extent, necessitating a repetition of the process.

The phenylhydrazine method is satisfactory, and, as Allen<sup>88</sup> says, it is especially useful when the object is to separate a very large amount of aluminum (1 mg. or even less) from a preponderating quantity of iron. This remark applies to titanium with still greater force. The execution of this process has already been given in sufficient detail under (1) (h).

#### (b) Titanium from Aluminum.

##### (\*) The Phosphate Process.

In a few preliminary experiments, Gooch<sup>89</sup> succeeded in making very good separations of 0.0373 gram of titanic oxide from 0.215 gram of aluminum oxide by adding a mixture of sodium ammonium phos-

phate and formic acid in the ratio of 5 grams of the phosphate to 8 grams of the acid to the solution till present in sufficient excess. The precipitate, which was formed in the cold, was found to be slimy and therefore difficult to filter. Because of indefiniteness on the part of titanium phosphate formed in this way, the precipitate was fused with sodium carbonate, the melt leached with water, the residual sodium titanate fused again with a little sodium carbonate, the mixture treated with sulfuric acid in the crucible, the syrupy solution diluted with water and the titanium thrown down again by the acetate hydrolysis (see p. 97).

Ericson<sup>90</sup> took up the matter of precipitating titanium as phosphate, and as the outcome of his experience claimed that from solutions containing either sulfuric or hydrochloric acid in regulated quantity it could be separated from its common associates with the exception of zirconium and tin.

Jamieson and Wrenshall<sup>91</sup> have investigated Ericson's process; and, in addition to those improvements already noted (pp. 88-9), they lay stress on the importance of having the acidity of the solution properly adjusted when separating titanium from aluminum. Their experiments show that from solutions of 100 cc. containing 0.05-0.15 gram of aluminum oxide not less than 8 cc. of hydrochloric acid (sp. gr., 1.18) may be present, if co-precipitation of aluminum is to be prevented, and that as much as 15 cc. of the acid does not exert any appreciable solvent action on the precipitate. They also add 1-2 grams of tartaric acid. It is thus evident that, when much aluminum is present, it is necessary to employ a somewhat higher concentration of hydrochloric acid than in the case of titanium and iron. Otherwise, the procedure is the same as that given under (4) (a) (\*\*\*\*\*) and (1) (b).

#### (\*\*) The Acetate Process.

Gooch,<sup>92</sup> having found the gelatinous precipitate of titanic phosphate very difficult to handle, next sought to accomplish the separation of titanium and aluminum by differential hydrolysis of the acetates. His experiments brought out the following interesting facts:—From a solution containing as much as 5 per cent of absolute acetic acid by volume aluminum shows no turbidity on boiling, and the addition of sodium acetate in reasonable amounts does not sensibly affect the result. On the other hand, precipitation of titanium is complete after a short period of boiling when 17.5 per cent of acetic acid is present along with somewhat more than enough sodium acetate to convert the sulfates to acetates. However, it is not advisable to employ so much acetic acid; since titanic acid falling from such a solution is of a consistency that renders it difficult to filter and wash; but within the range of from 7 to

11 per cent of said acid the precipitate comes down in flocculent and readily filterable condition. When, however, both titanium and aluminum are present, the first titanium precipitate occludes aluminum in considerable measure; and, if the amount of titanium is large, three precipitations may be necessary in order to obtain an aluminum-free product. It is less laborious and more satisfactory to fuse the precipitate with sodium carbonate and extract the melt with water, which incidentally removes phosphoric acid (should it happen to be present); and, having gotten the titanium back in solution in the manner given in (4) (b) (\*), to precipitate again by hydrolysis of titanic acetate. This precipitate is free from aluminum and the results of analysis are reasonably good. Additional details of procedure have been given under (4) (a) (\*) Optional Procedure No. 1.

(\*\*\*) The Cupferron Process.

No other known method for the separation of titanium and aluminum equals in simplicity and elegance the cupferron process. The experiments of Bellucci and Grassi<sup>98</sup> show that the separation is quantitative even when the weight of aluminum is twenty-eight times as great as that of the titanium. They do not give with sufficient exactness, however, the acidity of the solution, and the author<sup>94</sup> has demonstrated that this may not be too small; for, if so, aluminum contaminates the precipitate to a serious extent. If there be present 10 cc. of sulfuric acid (1:1) for every 100 cc. of the solution at the time the cupferron reagent is added, and if the solution contain also about 2.5 grams of tartaric acid, the separation is sharp and the results are accurate. The acid concentration may be greatly increased beyond that herein specified without causing any loss of titanium, as Lundell and Knowles<sup>95</sup> have pointed out; but in the author's opinion it will seldom be necessary to do this. The technique is exactly the same as that given under (1) (c).

According to J. Brown,<sup>96</sup> aluminum may be determined in the filtrate by evaporating to small bulk and destroying the nitrosophenyl-hydroxylamine with sulfuric and nitric acids in the usual way (cf. p. 97) and then precipitating with ammonium hydroxide in the manner recommended by W. Blum.<sup>97</sup>

The solution containing 5 grams of ammonium chloride per 200 cc. (or an equivalent amount of hydrochloric acid) is treated with a few drops of methyl red (0.2 per cent alcoholic solution) and heated just to boiling. Ammonium hydroxide is then added dropwise until the color changes to a distinct yellow.<sup>98</sup> The heating is resumed and the solution boiled for 1-2 minutes; whereupon the precipitate is collected on a filter paper and washed thoroughly with a hot 2 per cent solution of ammonium chloride (or nitrate). The moist paper and contents are



placed in a platinum crucible, dried and ignited—first over the Bunsen burner and finally over the blast lamp for 5 minutes. The covered crucible is weighed as rapidly as possible. After a second blasting of 5 minutes, the weighing is repeated and this value taken as correct.

(\*\*\*\*) **The Sodium Hydroxide Process (Aqueous Solution).**

The use of a large excess of sodium hydroxide in solution as a means of separating titanium and aluminum has been adversely criticized by Gooch<sup>99</sup> on the ground that titanous acid is markedly soluble in such a menstruum. Hillebrand<sup>100</sup> has confirmed this observation. However, Lundell and Knowles,<sup>101</sup> in some recent work on the estimation of zirconium in steel, separate the titanium and zirconium from aluminum by treating the cold solution having a volume of 300 cc. with 20 per cent sodium hydroxide, adding 10 cc. in excess.

A frequent objection that has been raised against the use of sodium hydroxide in refined analysis is that it is difficult to procure it of sufficiently good quality, aluminum being a common impurity.<sup>102</sup> Pure caustic alkalis may be prepared in the laboratory by the electrolytic method of H. P. Straus.<sup>103</sup> Furthermore, Lundell and Knowles<sup>104</sup> state that sodium hydroxide that is free from aluminum can now be obtained in the market.

(\*\*\*\*\*) **Fusion Processes.**

The old method of parting titanium and aluminum by fusing the oxides with sodium hydroxide in a silver crucible is open to much the same objections as the use of this reagent in the wet way, the titanium being even more soluble under these conditions. The aqueous extract from a sodium carbonate fusion, however, contains only a negligible trace of titanium. Some experiments by Hillebrand have brought out the curious fact that when much ferric oxide is present, with or without aluminum oxide, the solution of a sodium hydroxide melt contains practically no titanium; hence, it is permissible to make the fusion on material from which the iron has not yet been removed, but not on a mixture of aluminum and titanium oxides alone.

A similar procedure, due to L. Weiss and H. Kaiser,<sup>105</sup> consists in fusing the ignited oxides with twenty times their weight of a flux composed of sodium carbonate and sodium borate (borax) in equal parts. After thorough melting over the blast, half as much flux is again added and the fusion repeated. The cool melt is soaked in water for 24 hours. After filtration, a second fusion on the residue and subsequent extraction with water may sometimes be necessary. Weiss and Kaiser claim that aluminum is completely separated in this way from both iron and titanium.

## (c) Titanium from Phosphoric Acid.

A mixture of phosphoric acid and a titanic salt has for a long time been recognized by analysts as a somewhat difficult combination to handle. As already noted (p. 106), titanic phosphate is insoluble in rather strongly acid media; hence it is likely to appear at stages in the analysis when its presence would be distinctly objectionable. Furthermore, according to A. A. Blair's<sup>106</sup> observations, not only does phosphorus interfere with the estimation of titanium, but it is also true that titanium lowers the accuracy of the phosphorus determination.<sup>107</sup> In consideration of the above, it is perhaps best, in the analysis of phosphatic materials containing titanium, to separate the two during the preliminary treatment, as by fusion with sodium carbonate and a little sodium nitrate and extraction with water.<sup>108</sup> Details of procedure will be given under the analysis of titanium minerals.

As shown by the author's<sup>109</sup> experiments, titanium may be completely separated from very considerable quantities of phosphoric acid by cupferron, provided the solution contain sufficient amounts of sulfuric and tartaric acids. Results are given in Table VI.

TABLE VI.  
THE SEPARATION OF TITANIUM FROM PHOSPHORIC ACID.

TiO <sub>2</sub> Taken G.	P <sub>2</sub> O <sub>5</sub> Taken G.	TiO <sub>2</sub> Found G.	Error G.	H <sub>2</sub> SO <sub>4</sub> (1:1) Cc.	Tartaric Acid G.	Volume of Soln. Cc.
0.1064	0.0711	0.1071 <sup>a</sup>	+ 0.0007	20	1.5	400
0.1066	0.0710	0.1067	+ 0.0001	25	1.5	400

<sup>a</sup> Tested for P<sub>2</sub>O<sub>5</sub> and found to contain a trace.

It is evident from these figures that the separation is not quite complete when 20 cc. of sulfuric acid (1:1) is present in a volume of 400 cc. of the test solution. When, however, the sulfuric acid is increased by only 5 cc., the result is entirely satisfactory. Since these are by no means the uppermost permissible limits of either tartaric or sulfuric acid, it seems reasonably safe to assume that titanium may be readily separated from any amount of phosphoric acid that is at all likely to occur in either natural or technical products. It is a matter of no little interest and importance that cupferron is the only known precipitant for titanium that does not co-precipitate orthophosphoric acid. The technique of the separation has been given under (1) (c).

It is doubtless feasible to destroy organic matter in the filtrate and then precipitate the phosphoric acid with ammonium molybdate; but it is probably better in most cases to determine phosphorus in a separate

portion of the original sample, as will be described later under the analysis of minerals and technical products.

(d) Titanium from Iron, Aluminum and Phosphoric Acid.

From this group, which is so frequently obtained in mineral analysis, titanium may be readily separated by first precipitating the iron as ferrous sulfide according to (4) (a) (\*), removing hydrogen sulfide from the filtrate as described in (4) (a) (\*) Optional Procedure No. 3 and then precipitating the titanium with cupferron as directed in (1) (c).

The same object may be attained by the method of Gooch,<sup>110</sup> either in its original form or as modified by T. M. Chatard;<sup>111</sup> or, if preferred, Blair's<sup>112</sup> procedure may be followed; but in the author's opinion these processes are inferior in point of convenience and probably less accurate than the cupferron method as outlined above.

(e) Titanium from Chromium and Vanadium.

Cupferron does not precipitate trivalent chromium from acidified solutions, as H. Biltz and O. Hödtke<sup>113</sup> have shown; hence there should be no difficulty attending the separation of titanium from chromium.

With vanadium, however, the case is different. Lundell and Knowles<sup>114</sup> record experiments wherein the precipitate of a mixture of titanium and zirconium (produced by cupferron) was found to contain very noteworthy amounts of vanadium; though the occlusion is much less when the vanadium is present in the quadrivalent than in the quinquevalent state. Moreover, F. J. Pope<sup>115</sup> has obtained similar results when precipitating titanium by the acetate process in the presence of sulfurous acid.<sup>116</sup>

All things being considered then it seems best to separate both chromium and vanadium from titanium (as well as from iron and other substances) in the manner prescribed by Hillebrand.<sup>117</sup> This consists in fusing the dry sample with four times its weight of sodium carbonate and three fifths of its weight of sodium nitrate and extracting the melt with water. Sodium chromate and vanadate enter the filtrate while sodium titanate remains as an insoluble residue. This procedure will be given in detail under the analysis of titanium minerals.

Another method for separating vanadium from titanium, which has been employed by P. W. and E. B. Shimer,<sup>118</sup> is to fuse one part of the finely powdered substance with four parts of sodium carbonate and four parts of sulfur in a porcelain crucible at a comparatively low temperature. On leaching the mass with water, the vanadium goes into solution, presumably as sodium thiovanadate, while titanium remains

behind. The vanadium may be determined by acidifying the cold filtrate with sulfuric acid, collecting the precipitated vanadium sulfide on paper, incinerating in a porcelain crucible, dissolving the vanadium pentoxide in hydrochloric acid (sp. gr., 1.20) and evaporating nearly to dryness, renewing the hydrochloric acid and evaporating again with the addition of sulfuric acid to the fuming point of the latter and finally titrating the divanadyl sulfate with potassium permanganate.<sup>119</sup> The titaniferous residue is treated with dilute sulfuric acid, which readily dissolves any ferrous sulfide, and the portion insoluble in dilute acid is fused with potassium bisulfate and a little sodium fluoride and the melt taken up with dilute sulfuric acid (about 10 per cent by volume). The two solutions are united, since the former is liable to contain a small part of the titanium, and the titanium is estimated in such manner as may be desired.

#### (f) Titanium from Manganese, Cobalt, Nickel and Zinc.

Recent experiments by Lundell and Knowles<sup>120</sup> have demonstrated that titanium (along with aluminum and iron) may be quantitatively separated from manganese by simple precipitation with ammonium hydroxide, provided the directions of Blum (p. 107) be carefully followed.

To separate titanium from all the metals of this group either the barium carbonate method<sup>121</sup> or acetate hydrolysis in the presence of sulfurous acid (pp. 105 and 106) may of course be employed.

Since, however, cupferron does not precipitate manganese, cobalt, nickel or zinc,<sup>122</sup> the technique of (1) (c) could be utilized here to yield separations of great nicety.

#### (g) Titanium from Zirconium.

The separation of titanium and zirconium was for a long time looked upon as a difficult analytical problem. J. J. Berzelius<sup>123</sup> attempted to solve it as early as 1826; and, although the matter was investigated by several chemists<sup>124</sup> in the mean time, it cannot be said that a really satisfactory method was known prior to the work of Hillebrand.<sup>125</sup>

Having found that G. H. Bailey's<sup>126</sup> proposal to separate zirconium from titanium (as well as from iron, columbium, tantalum, tin, silicic acid, etc.) by adding strong hydrogen peroxide to the slightly acidified solution failed to yield a precipitate of zirconium except from very concentrated solutions, Hillebrand<sup>127</sup> took recourse to the use of a soluble phosphate as the precipitant for zirconium while holding up titanium with an excess of the peroxide. The permissible acidity has been found to be much greater than that originally prescribed by Hillebrand (not

much more than 1 per cent of sulfuric acid). G. Steiger<sup>128</sup> has shown that 3-5 per cent of sulfuric acid by weight is compatible with total precipitation, and P. Nicolardot and A. Réglade<sup>129</sup> have been able to increase this to 20 per cent (by weight). Indeed the higher acidity prevents contamination of the precipitate by titanium, iron and chromium. The method of Hillebrand has been thoroughly studied, more particularly by Lundell and Knowles,<sup>130</sup> who have established the most favorable conditions for its application; hence it is in all probability the most reliable process for estimating zirconium in the presence of titanium<sup>131</sup> and more broadly for the analysis of zirconiferous materials in general.

(\*) **The Phosphate Process.**

The solution, which should occupy a volume ranging from 25 cc. for small amounts (0.0005 gram of zirconium oxide) to 200 cc. for larger amounts (0.1 gram) and contain 20 per cent of sulfuric acid by weight, is treated with 10 cc. of hydrogen peroxide (3 per cent solution) and maintained at a temperature of 40-50°C. From ten to one hundred times the theoretical quantity of ammonium phosphate is then added—the larger excess being indicated when small amounts of zirconium are to be determined—and, after thorough stirring, the beaker is set aside for the precipitate to settle. Two hours is enough for the complete precipitation of any amount of zirconium dioxide exceeding 0.005 gram; but for smaller amounts 6 hours or even longer may be required. As much as possible of the supernatant liquid is decanted through a filter of close texture so as to avoid clogging, and the precipitate is washed with a cold 5 per cent solution of ammonium nitrate. The precipitate is ignited carefully in a partially covered platinum crucible, the flame being kept low until all carbon is consumed; when it is brought to constant weight over the blast lamp. Under these conditions zirconium pyrophosphate is definitely obtained, which may be converted to zirconium dioxide by multiplying the weight by 0.4632.

Brown and Madden<sup>132</sup> have shown that titanium may be determined in the filtrate from the zirconium phosphate by precipitating it too as phosphate. The solution is first boiled to decompose hydrogen peroxide. The acidity is then adjusted to about 2 per cent of sulfuric acid by volume and more ammonium phosphate is added if necessary. The titanium phosphate is of variable composition. It is therefore fused with sodium carbonate, the melt leached with water and the residue dissolved either with hydrochloric acid or by fusion with sodium bisulfate and subsequent digestion in dilute sulfuric acid. The titanium is finally thrown down by ammonium hydroxide and ignited to titanous oxide.

(\*\*) The Salicylate Process.

M. Dittrich and S. Freund<sup>133</sup> have based a separation of titanium and zirconium on the difference in solubility of their respective salicylates.

The solution of the nitrates (previously neutralized with sodium carbonate) is let fall dropwise from a separatory funnel into a boiling solution of 10 grams of ammonium salicylate in 50 cc. of water. Titanium salicylate passes into solution, imparting a yellow color to the liquid, while zirconium forms a white precipitate of ammonium zirconium salicylate, which is quite insoluble under the conditions. The solution is heated for some time, the volume being kept within 150-200 cc. The precipitate is filtered off as hot as possible and washed with a boiling strong solution of ammonium salicylate until it appears white or at most shows only a pale yellow tint. The precipitate is ignited in a platinum crucible, blasting to constant weight, and the zirconium determined as dioxide. If the precipitate, after fusion with sodium pyrosulfate, shows titanium on being tested with hydrogen peroxide, the precipitation should be repeated. For this purpose the zirconium is precipitated with ammonium hydroxide and redissolved in the least possible quantity of nitric acid and the above procedure gone through with again. It is simpler, however, to estimate the small amount of titanium colorimetrically and then correct the weight of zirconium oxide accordingly.

To determine the titanium the yellow or orange filtrate is treated at the boiling temperature with a large excess of ammonium hydroxide and heated for a long time. In this way the solution is bleached and a flocculent precipitate of titanous acid separates out, which is collected and ignited in the ordinary manner. The titanous oxide should be tested for a small content of silicic acid, in case the analysis has been performed in glassware.

(\*\*\*) The Selenite Process.

M. M. Smith and C. James<sup>184</sup> have introduced selenious acid as a precipitant for zirconium. Through its agency most of the substances that accompany zirconium in nature may be separated from it—phosphoric acid being an exception. In the case of titanium, however, it is necessary to have present also a considerable quantity of hydrogen peroxide.

The solution of the chlorides, containing 10 cc. of hydrochloric acid (sp. gr., 1.19), is treated with hydrogen peroxide in some excess and the volume made up with water to 500 cc. Aqueous selenious acid (about 12.5 per cent) is then added to the cold solution, 10 cc. being used for each 0.1 gram of zirconium oxide. The precipitate is filtered

off, washed with water containing 2 per cent of hydrochloric acid and a little selenious acid and ignited to zirconium dioxide.

(\*\*\*\*) **The Arsenate Process.**

Still more recently, L. Moser and R. Lessnig<sup>135</sup> have brought out the separation of zirconium (and hafnium) from titanium, cerium and thorium by means of disodium arsenate. On adding the reagent to a nitric acid solution of zirconium a white insoluble zirconyl salt,  $ZrO.HAsO_4$ , is formed, which is dense and readily filtered. Titanium, in the presence of hydrogen peroxide, remains in solution.<sup>136</sup> The precipitate is dissolved in concentrated sulfuric acid, hydrochloric acid and hydrazine are added and the arsenic distilled off as trichloride. The residual solution is diluted and the zirconium precipitated with ammonium hydroxide. The first precipitate is redissolved in dilute hydrochloric acid and the precipitation repeated. The zirconium hydroxide is collected and ignited in the usual manner.

Titanium may be recovered from the filtrate by introducing sulfur dioxide to destroy the hydrogen peroxide and then precipitating with ammonium hydroxide.

(\*\*\*\*\*) **The Ammonium Fluoride Process.**

Another method for separating titanium and zirconium is that of W. P. Headden.<sup>137</sup> This process seems to have been thus far overlooked by compilers; but the satisfactory results obtained by Headden are sufficient to warrant its description here.

The acid solution containing the elements in question is first neutralized with ammonium hydroxide, a slight excess doing no harm, and then ammonium fluoride is added until the precipitate produced by the former reagent has gone back into solution. It is advisable to have present a moderate excess of the ammonium fluoride. If now ammonium hydroxide be added in some excess to the boiling solution and the ebullition continued for about one minute, the titanium is completely precipitated as an easily filterable form of titanous acid.

The filtrate contains all of the zirconium, from which it may be obtained by adding a little more than enough sulfuric acid to convert the ammonium salts into sulfates, evaporating to dryness and fusing the mass until all fluorine has been expelled, taking up with water and precipitating with ammonium hydroxide in the usual way.

(\*\*\*\*\*) **The Co-precipitation of Titanium and Zirconium and the Volumetric Estimation of Titanium.**

As Hillebrand<sup>138</sup> has pointed out, zirconium prevents the complete precipitation of titanium under the conditions of the Gooch method

(q.v.). This is not so with the cupferron process (p. 90), wherein both titanium and zirconium are quantitatively thrown down. Since zirconium does not exhibit a valence lower than four, it is obviously feasible to redissolve the ignited and weighed precipitate by suitable means (e.g., fusion with potassium pyrosulfate) and determine the titanium either oxidimetrically or colorimetrically according as its amount is large or small. The zirconium is thus arrived at by difference. Of course this procedure is not to be recommended when a very small amount of zirconium accompanies a large amount of titanium; but the reverse state of affairs would always prevail in zirconium ores.<sup>139</sup> The volumetric methods for estimating titanium will be fully described further on.

#### (h) Titanium from Columbium and Tantalum.

Columbium and tantalum resemble each other so closely in chemical behavior that it will be convenient to consider them together in the present discussion. Most of the methods that have thus far been devised for separating titanium from either columbium or tantalum leave much to be desired in point of accuracy; but the difficulties involved in handling this combination of elements are so great that the want of better procedures is not at all surprising. By way of a preliminary survey of the matter, those salient properties of the acid-earths, which have been most often utilized as bases of differentiation, are set forth briefly in Table VII. It must be borne in mind, however, that while certain elements behave quite differently when alone they may show a great change in deportment in the presence of one another—the basis of distinction being in large measure lost.<sup>140</sup> It is thus stated in several texts<sup>141</sup> that, on leaching the mass obtained after a potassium bisulfate fusion with cold water, titanium goes into solution while columbium and tantalum remain undissolved. But when the three elements are present in admixture, a large part (if not all) of the columbium and tantalum pass into solution along with the titanium, as Headden<sup>142</sup> has observed.

In the following sections only a few of the more promising methods of separation will be described. A more complete collection of processes may be found in the work of R. J. Meyer and O. Hauser.<sup>143</sup>

#### (\*) The Chloride Process.

A. Knop<sup>144</sup> was the first to suggest the separation of titanium from columbium and tantalum dependent upon the difference in volatility of the chlorides. The oxides are mixed with carbon and heated red-hot



TABLE VII.  
SOME ANALYTICAL CHARACTERISTICS OF THE ACID-EARTHS.  
(Ti, Cb and Ta)

Property	Ti	Cb	Ta
Sp. gr. of oxides.....	TiO <sub>2</sub> 4.25	Cb <sub>2</sub> O <sub>5</sub> 4.55	Ta <sub>2</sub> O <sub>5</sub> 8.72
B. Pt. of chlorides, ° C.....	TiCl <sub>4</sub> 136	CbCl <sub>5</sub> 245	TaCl <sub>5</sub> 242
Solubility of potassium salts of fluo- acids in 100 parts of water.....	K <sub>2</sub> TiF <sub>6</sub> . H <sub>2</sub> O 1.28	K <sub>2</sub> CbOF <sub>5</sub> . H <sub>2</sub> O 7.7-8.3	K <sub>2</sub> TaF <sub>7</sub> 0.64-0.66
Solubility of K <sub>2</sub> S <sub>2</sub> O <sub>7</sub> melt in water....	Soluble	Insoluble	Insoluble
Solubility of potassium salts in salicylic acid .....	K <sub>2</sub> TiO <sub>3</sub> soluble	K <sub>2</sub> Cb <sub>2</sub> O <sub>10</sub> insoluble	K <sub>2</sub> Ta <sub>2</sub> O <sub>10</sub> insoluble
Solubility of oxides in SeOCl <sub>2</sub> and H <sub>2</sub> SO <sub>4</sub> .....	TiO <sub>2</sub> soluble	Cb <sub>2</sub> O <sub>5</sub> soluble	Ta <sub>2</sub> O <sub>5</sub> insoluble
Action of H <sub>2</sub> O <sub>2</sub> on H <sub>2</sub> SO <sub>4</sub> solution....	TiO <sub>2</sub> orange	Cb <sub>2</sub> O <sub>5</sub> colorless	Ta <sub>2</sub> O <sub>5</sub> colorless
Zn and H <sub>2</sub> SO <sub>4</sub> .....	Ti <sub>2</sub> O <sub>3</sub> violet	Cb <sub>2</sub> O <sub>3</sub> brown	Ta <sub>2</sub> O <sub>5</sub> colorless

in a combustion tube while a current of chlorine is being maintained. The lower boiling titanium tetrachloride (Table VII) is collected in a receiver and the columbium and tantalum pentachlorides are condensed on the forward portion of the tube. Both R. D. Hall<sup>145</sup> and O. Hauser<sup>146</sup> report unsatisfactory experiences with this process.

O. Ruff and E. Schiller,<sup>147</sup> on the other hand, claim that by substituting carbon tetrachloride for elemental carbon good results may be obtained under certain specified conditions.

F. L. Hess and R. C. Wells,<sup>148</sup> in applying this method to the analysis of strüverite (Table I), employed chloride of sulfur as the reducing agent, and warmed the forward part of the tube to 70-80°C. By proceeding in this way, they found the condensate of less volatile chlorides to be practically free from titanium but that the solution in the wash bottles used to collect the titanous chloride contained appreciable amounts of columbium and tantalum. On recovering the impure titanium in the form of its oxide and subjecting it to a repetition of the above treatment they were able to separate nearly all the columbium and tantalum from the titanium.

**(\*\*) The Salicylate Process.**

The solubility of titanium salicylate in a hot solution of alkali salicylate and the insolubility of zirconium salicylate under the same conditions, as utilized by Dittrich and Freund<sup>149</sup> for the separation of zirconium and titanium, led Hauser and Herzfeld<sup>150</sup> to experiment along similar lines with a view to separating titanium from columbium and tantalum in connection with the analysis of blomstrandite (Table I). In like manner J. H. Muller<sup>151</sup> has brought out a process, which he describes in some detail, and concerning which he claims that the separations are satisfactory.<sup>152</sup>

The mixture of oxides, varying from 0.3 to 0.7 gram, is fused with 5 grams of potassium carbonate, the melt extracted with 350-400 cc. of water at 60°C., 14-15 grams of salicylic acid added and the solution heated 3-4 hours at the boiling temperature. The precipitate is allowed to settle, filtered rapidly and washed with boiling water. These operations may have to be repeated several times to remove the titanium completely from the residual acid-earths. The precipitate of columbium and tantalum occludes alkali salicylate that is not entirely eliminated by washing. It is therefore redissolved by means of a bisulfate fusion, and the oxides are recovered in the usual manner.

Titanium may be estimated in the combined filtrates by concentrating and precipitating with ammonium hydroxide.

**(\*\*\*) The Selenium Oxychloride Process.**

H. B. Merrill<sup>153</sup> has proposed to separate columbium from tantalum by treating the oxides with a hot mixture (1:1) of selenium oxychloride and concentrated sulfuric acid, the columbium being much more readily soluble in this menstruum. Contrary to the general rule, titanium accompanies the columbium. No experimental data are given for titanium, and the test analyses on known mixtures of columbium and tantalum leave a good deal to be desired; but the process is doubtless superior to the classical method of C. Marignac.<sup>154</sup>

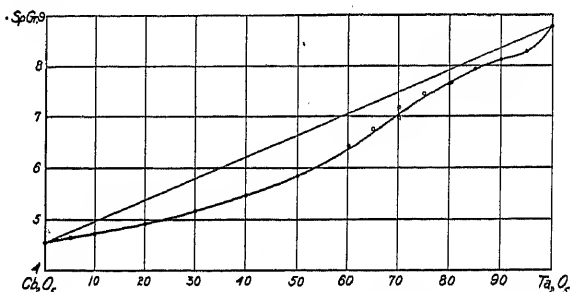
**(\*\*\*\*) The Co-precipitation of the Acid-earths and the Colorimetric Determination of Titanium.**

Since there is no development of color on adding hydrogen peroxide to a solution of either columbium or tantalum, the method of A. Weller<sup>155</sup> may be conveniently used for estimating the titanium when present in relatively small amounts. As the amount of titanium increases the results become less and less accurate so that very large quantities can only be approximated in this way. The colorimetric determination of titanium will be fully described in Chapter VII.

(i) The Estimation of Columbium and Tantalum in the Presence of Each Other.

Granting that titanium has been completely separated from columbium and tantalum by one of the processes outlined above, the determination of these two elements, which practically always accompany each other in nature, remains as one of the most difficult of analytical problems.

The well-known method of Marignac,<sup>156</sup> which is based upon the greater solubility in water of potassium oxyfluocolumbate as compared with potassium fluotantalate, is tedious and at best can only lead to approximate results. The Marignac process is given in great detail by J. W. Mellor.<sup>157</sup>



(H. W. Foote and R. W. Langley: *American Journal of Science*, ser. 4, vol. 30, p. 393, 1910.)

FIG. 14.—Specific gravities of mixtures of columbic and tantalic oxides.

An indirect and probably more accurate method is that of H. W. Foote and R. W. Langley,<sup>158</sup> which depends upon determining the specific gravity of the mixture of columbium and tantalum oxides and then finding the percentage composition by reference to an empirically plotted curve (Figure 14). The way in which the oxide mixture has been treated prior to the specific gravity determination makes a considerable difference in the density; hence the oxides must be prepared under rigidly fixed conditions.

The differential solvent action on the oxides of sulfuric acid containing selenium oxychloride, as proposed by Merrill,<sup>159</sup> has already been mentioned (p. 117).<sup>160</sup>

The oxidimetric determination of columbium by reduction with zinc to a lower valence and subsequent titration with potassium permanganate was first brought out by T. B. Osborne.<sup>161</sup> Tantalum remains unaffected throughout these operations and may therefore be arrived at by the method of difference. Osborne's process is thought to be very imperfect partly because of incomplete reduction of the columbium to

the trivalent state and partly because of inadequate protection of the deoxidized solution prior to titration.<sup>162</sup> F. J. Metzger and C. E. Taylor,<sup>163</sup> by proceeding in a purely empirical way, established a titrimetric method, which is probably more accurate than that of Osborne. The procedure follows:

The mixture of oxides (corresponding to from 0.2 to 1.0 gram of the mineral) is fused with 5 grams of potassium bisulfate in a platinum crucible. Ten cc. of sulfuric acid (sp. gr., 1.84) is added to the cooled melt and the crucible warmed until a clear solution is obtained, which is transferred to a beaker, the crucible being rinsed with 30 cc. of the same acid. The solution should be perfectly clear at this stage—cloudiness indicating incomplete fusion. Two grams of succinic acid is now added and the liquid stirred for a short time, about 20 cc. of a saturated solution of succinic acid is also introduced in a fine stream with constant agitation, and after making up the volume with water to 200 cc. the solution is heated to 75°C. Meanwhile a Jones reductor (19 inches by  $\frac{3}{4}$  inch), which has been charged with slightly amalgamated zinc (see below), is prepared by passing through it 200 cc. of sulfuric acid (5 per cent) heated to 75°C., rejecting this and filling again with 20 per cent acid likewise heated to 75°C. The test solution is now passed through the reductor, followed by 50 cc. of sulfuric acid (20 per cent), and the tube is washed with 200 cc. of sulfuric acid (5 per cent)—the receiving flask being filled with carbon dioxide. The reduced solution is titrated promptly with potassium permanganate, which is delivered from a burette with extra long stem. The permanganate should be standardized against a weighed quantity of pure columbium pentoxide under exactly the same conditions.

The amalgamating solution is prepared by dissolving 0.5 gram of mercury in 25 cc. of nitric acid (sp. gr., 1.42) and diluting to 250 cc. with water. Six hundred grams of zinc (20-30 mesh) is immersed in the nitrate of mercury solution and the two are shaken together for several minutes. The coated zinc is washed first with water and then with dilute sulfuric acid. It is then kept under water till needed. Having charged this material into the reductor,<sup>164</sup> a blank experiment is made in the manner described above and the main titer corrected accordingly.

Although the method of Metzger and Taylor has been unfavorably criticized by several investigators,<sup>165</sup> it seems to have afforded reasonably good service in the hands of E. W. Todd.<sup>166</sup> The value obtained by Todd (0.00709 gram) for 1 cc. of 0.1 N potassium permanganate in terms of columbium pentoxide is not very different from that of Metzger and Taylor (0.00705 gram). It is interesting to note that the oxides isolated by Todd from the various minerals were not entirely

free from titanium. This titanium was therefore determined colorimetrically in an aliquot part of the test material. An equal quantity of titanium was then taken from a standard solution of titanous sulfate and put through all the steps of the Metzger and Taylor process. A correction to the titer for columbium could thus be applied; and, the titanium and columbium in the precipitate being known, the tantalum could be obtained by difference.

Still other chemists<sup>107</sup> have studied the volumetric estimation of columbium; but it would seem that their work adds little to that already given. With the exception of Osborne, all agree in saying that the reduction of the columbium, under any conditions thus far discovered, does not go as far as the trivalent state and that the process is empirical and subject to some uncertainty. However, the volumetric procedure is superior in point of convenience and scarcely less accurate than most of the gravimetric methods now in vogue.

#### (j) Titanium from Thorium.

##### (\*) The Oxalate Process.

The nearly neutral solution of the chlorides is treated with ammonium oxalate until the precipitate which forms at first has redissolved. The solution is then heated to boiling, and hydrochloric acid is added dropwise till no further precipitation takes place. After standing overnight the thorium oxalate is collected on a filter and thoroughly washed with warm water containing hydrochloric acid.<sup>108</sup>

The titanium may be obtained from the filtrate by evaporating with sulfuric acid to the fuming point, cooling, diluting with water and precipitating with ammonium hydroxide.<sup>108</sup>

##### (\*\*) The Fluoride Process.

The nearly neutral solution of the sulfates is treated with dilute hydrofluoric acid and warmed until the thorium fluoride becomes dense. The precipitate is filtered off, using a paper filter set in a hard rubber funnel and receiving the filtrate in a platinum basin, and well washed with a very dilute solution of hydrofluoric acid.<sup>109</sup>

##### (\*\*\*) The Double Sulfate Process.

The hydrochloric or sulfuric acid solution is rendered as nearly neutral as possible without causing the formation of a permanent turbidity by the careful addition of potassium hydroxide. Solid potassium sulfate is then introduced until crystals remain undissolved on the bottom of the vessel, showing that the solution is really saturated with respect to that salt. Thorium comes down as the double sulfate,

$\text{K}_4\text{Th}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ , while titanium remains in solution. The precipitate is washed with a cold saturated solution of potassium sulfate.<sup>170</sup>

(\*\*\*\*) **The Salicylate Process.**

Dittrich and Freund<sup>171</sup> have shown that titanium may be separated from thorium in exactly the same manner as from zirconium through the agency of ammonium salicylate. The technique has already been given in (4) (g) (\*\*).

(k) **Titanium from the Rare Earths.**

The oxalate and fluoride precipitations, which have just been described, will also serve for the separation of titanium from the rare earth elements in general. Moreover, the double sulfate process may be used to separate it from the members of the cerium group (cerium, lanthanum, neodymium, praseodymium, etc.) as well as from thorium. From the yttrium group (yttrium, erbium, etc.) it may be separated by boiling the dilute and slightly acidified sulfuric acid solution or by hydrolysis in the presence of an alkali acetate—titanic acid being precipitated and the yttrium earths remaining in solution.<sup>172</sup>

(l) **Titanium from Uranium.**

H. Brearley<sup>173</sup> separates titanium from uranium by treating the hot solution with a rather large quantity of acetic acid and then with enough ammonium acetate to react with the free mineral acid—a large excess of the acetate being avoided. He also suggests the use of sodium thio-sulfate under similar conditions.

Lundell and Knowles<sup>174</sup> have shown that both titanium and zirconium can be separated from uranium in the hexavalent state (uranyl salts) by precipitating with cupferron in a solution containing 10 per cent of sulfuric acid by volume and 1 gram of tartaric acid. Quadri-valent uranium (uranous salts), however, interferes by being co-precipitated to a considerable extent; in fact, J. A. Holladay and T. R. Cunningham<sup>175</sup> have demonstrated that from solutions containing 2-8 cc. of sulfuric acid (sp. gr., 1.84) in 100 cc. uranium in the quadri-valent condition (or lower) is completely thrown out by the cupferron reagent. Since the test analyses of Lundell and Knowles are entirely satisfactory, it would seem that the use of cupferron constitutes the simplest and best method for performing this separation.

(m) **Titanium from Beryllium.**

Lundell and Knowles<sup>176</sup> have in like manner found that beryllium is not precipitated by cupferron from solutions containing 10 per cent

by volume of sulfuric acid and also some tartaric acid either alone or when mixed with titanium and zirconium; hence the separation of titanium from beryllium should involve no difficulty.

#### (n) Titanium from Gallium.

Though it seems improbable that the very rare element gallium would occur in titaniferous materials in appreciable amounts, L. de Boisbaudran,<sup>177</sup> the discoverer of gallium, has given five methods for separating it from titanium. The most generally applicable is founded upon the action of a boiling solution of potassium hydroxide. The gallium hydroxide, which first forms, redissolves in an excess of the precipitant while titanic acid remains unaffected.

#### (5) THE SEPARATION OF TITANIUM FROM THE COPPER AND TIN GROUPS.

According to F. P. Treadwell<sup>178</sup> hydrogen sulfide precipitates from a solution which is 0.3 N in acid only the metals of the "hydrogen sulfide group". It is better to employ sulfuric acid as the acidifying agent in the present case; since sulfate solutions of titanium are more stable than chloride solutions. Besides this general method special procedures are used for separating titanium from certain of the hydrogen sulfide metals.

##### (a) Titanium from Copper.

L. Lévy<sup>179</sup> states that titanium is separated from copper by the hydrolysis of titanic sulfate. Lévy's conditions are the same as those given in (1) (d).

Titanium may also be precipitated free from copper by working with a chloride solution in the manner recommended by Baskerville.<sup>180</sup> See (1) (e) and (4) (a) (\*\*\*\*\*).

##### (b) Titanium from Tin.

There seems to be only one specific process in the literature for separating titanium and tin, viz., that of A. Hilger and H. Haas;<sup>181</sup> though several other procedures have been applied to the estimation of tin in certain titanium bearing minerals.<sup>182</sup>

In the Hilger and Haas method the mixture of the oxides is heated to low redness in an atmosphere of hydrogen. The oxide of tin is reduced to the metal. After cooling in hydrogen the mass is extracted with 20 per cent hydrochloric acid at the boiling temperature. The tin in the filtrate is then precipitated by hydrogen sulfide and the precipitate is collected and finally converted to stannic oxide for weighing.

The experimental data obtained by Hilger and Haas on artificial mixtures are reasonably good. On applying the method directly to strüverite, however, Hess and Wells<sup>183</sup> found less tin than by any of the three other procedures tried, which would indicate that there may be some doubt concerning the completeness with which the tin is extracted.

#### (c) Titanium from Molybdenum.

Titanium may be parted from molybdenum by fusing the dry sample with sodium carbonate and sodium nitrate and extracting the melt with water as in the case of chromium and vanadium. See (4) (e).

Another possibility is to throw down molybdenum trisulfide by passing hydrogen sulfide into a nearly neutral sulfate solution containing tartaric acid.<sup>184</sup>

#### (d) Titanium from Tungsten.

E. Defacqz<sup>185</sup> has based a separation of tungsten and titanium upon fusing the material with potassium nitrate and potassium carbonate.

The tungstic acid, as ordinarily obtained in analysis, occludes a part of the titanium originally present. After volatilizing the silicon dioxide, the residue is fused with sodium carbonate and leached with water. Sodium tungstate passes into solution and sodium titanate remains behind with the other impurities.<sup>186</sup>

### (6) THE SEPARATION OF TITANIUM FROM THE SILVER GROUP.

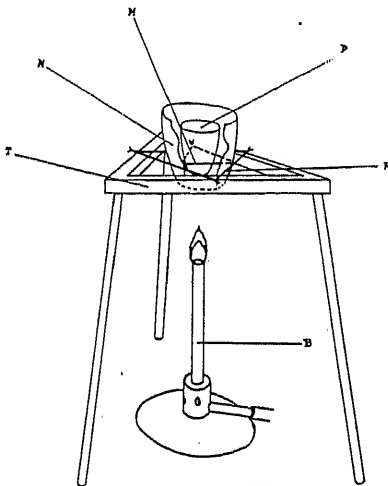
These metals, which form insoluble chlorides, are not likely to accompany titanium either in natural or technical products. Since titanous chloride is freely soluble in water, there should be no difficulty in precipitating silver as chloride from a nitrate solution. Of the other metals, mercury and lead have been provided for in (5), and thallium is too rare to warrant consideration.

### (7) THE SEPARATION OF TITANIUM FROM SILICIC ACID.

Whether the silicic acid should be rendered insoluble by evaporation with hydrochloric acid at the water bath temperature or with sulfuric acid at its fuming point will depend upon the way in which the original material has been decomposed. Highly silicious bodies are best opened up by fusion with sodium carbonate, disintegration of the melt with water and treatment with hydrochloric acid. The oxides (rutile, ilmenite, etc.) are preferably fused with potassium pyrosulfate and the resulting mass digested with sulfuric acid. Titanium alloys, as a general rule, are completely attacked by acids, the more volatile of



which are removed by evaporation with sulfuric acid. Still other methods of decomposition may be found useful in special cases.<sup>187</sup> Dehydration with sulfuric acid, whenever permissible, has certain advantages: only one evaporation is necessary, whereas two are required when hydrochloric acid is used, and the silicic acid so obtained suffers less contamination by the titanium. In either case it is important to wash the paper containing the residue very thoroughly so as to get rid of all alkali salt. The washing fluid may be water or very dilute acid and either may be applied cold or hot—all according to circumstances. After ignition, the exact determination of silicon dioxide is accom-



(W. M. Thornton, Jr.: *Journal of Industrial and Engineering Chemistry*, vol. 3, p. 419, 1911.)

FIG. 15.—Nickel crucible radiator.

plished by volatilization of silicon fluoride and noting the loss in weight. It is a well known fact that during the evaporation of hydrofluoric acid titanium fluoride (and certain other fluorides as well) is noticeably volatilized but that, if sulfuric acid be present in sufficient quantity, no such loss is incurred. Experiments by P. Holland<sup>188</sup> show that in the presence of 2 cc. of sulfuric acid (5 cc. = 0.8 gram  $\text{SO}_3$ ) as much as 0.052 gram of titanic oxide undergoes no change of weight as a result of the operation. The residue in the platinum crucible is moistened with 1-2 cc. of water, from 1 to 10 drops of concentrated sulfuric acid are added depending upon the amount of titanium present, 5-10 cc. of hydrofluoric acid (48 per cent) introduced and the whole evaporated to dryness over a ring burner or in some suitable form of radiator. The

crucible is ignited very carefully at first, with the lid set so as to leave a small opening, the heat gradually increased and finally the Méker burner applied until a constant weight is obtained. The non-volatile matter may be redissolved by fusing it with a little potassium pyrosulfate and treating the melt with dilute sulfuric acid. This is added to the main solution, which will then contain all of the titanium.

A very simple form of radiator has been devised by the author,<sup>189</sup> by means of which liquids may be evaporated to dryness without danger of loss by spattering and with no great expenditure of time. It is made from a nickel crucible of 100 cc. capacity (or larger) and a 1½ inch nichrome triangle. The ends of the triangle are cut off at points about midway their length and bent upwards. This triangle M (Figure 15) is supported by the walls of the nickel crucible N at a height that will hold the platinum crucible P with its bottom and sides about equidistant from the bottom and sides of the nickel crucible. With proper adjustment of the flame evaporation takes place quietly but rapidly from the surface of the liquid without the slightest ebullition. The time required varies somewhat according to circumstances, depending especially upon the quantity of sulfuric acid added and the amount of the solid residue; but in the normal case of silicon determination, with the bottom of the nickel crucible maintained at a low red heat, the contents of the platinum crucible will become dry in about 1 hour. In order that the operation may demand as little of the analyst's time as possible, it is well to employ a flame too low to vaporize the sulfuric acid until practically all of the hydrofluoric acid has been expelled; whereupon the temperature is cautiously increased up to the point at which the sulfuric acid smokes off slowly.

#### (8) THE SEPARATION OF TITANIUM FROM BORIC ACID.

W. M. Bradley,<sup>190</sup> in his analysis of warwickite (Table I), separated boric acid from titanium in the following manner: The finely powdered mineral is fused with sodium carbonate, the mass is extracted first with water and then with hot sodium carbonate solution and the residue is thoroughly washed with water containing a little sodium carbonate. These operations are repeated several times. Eventually a filtrate is obtained that contains all of the boron and only a trace of titanium. The boric acid is then distilled with methyl alcohol according to the method of Gooch,<sup>191</sup> absorbed in ammonium hydroxide and evaporated in contact with calcium hydroxide. The small amount of titanium remaining in the still may be added to the main residue and the total amount of titanium estimated by any desired procedure.<sup>192</sup>

Titanium may be separated from boric acid in a much simpler way, as Lundell and Knowles<sup>198</sup> have shown, by making use of the cupferron reagent. The solutions employed by them contained 40 cc. of sulfuric acid (1:1) and 1 gram of tartaric acid in a volume of 400 cc. Zirconium is precipitated free from boric acid under the same conditions.

## Chapter VII.

### Colorimetric Methods.

#### (1) THE DETERMINATION OF TITANIUM WITH HYDROGEN PEROXIDE.

##### (a) General Discussion.

The yellow or orange color that develops when hydrogen peroxide is added to a solution of a titanium salt was first observed by H. v. Schönning,<sup>1</sup> but credit is due A. Weller<sup>2</sup> for having utilized the phenomenon as the basis of a quantitative process. The method consists briefly in comparing the color of the solution under examination with that of a solution containing a known quantity of titanium per unit volume and similarly treated. Sulfuric acid solutions are generally employed; though hydrochloric acid solutions from which the iron has been removed may be used, provided the standard solution be composed of titanium chloride also.<sup>3</sup> As F. P. Dunnington<sup>4</sup> has pointed out, the complete development of color does not take place unless a sufficient quantity of sulfuric acid be present. Dunnington attributes this to the formation of some metatitanic acid which does not react with hydrogen peroxide; but P. Faber<sup>5</sup> considers that it is due to the presence of basic titanic sulfate. L. Weiss and H. Kaiser<sup>6</sup> in turn do not accept Faber's explanation. At all events, it is advisable to have present at least 5 cc. and preferably 10 cc. of sulfuric acid (sp. gr., 1.84) for every 100 cc. of the solution. It must of course be understood that the colorimetric methods are applicable only to the estimation of small amounts of titanium. Whenever the titanium content of the sample (reckoned as titanium dioxide) exceeds 4 or 5 per cent, recourse should be had to a gravimetric or oxidimetric process. An exception to this rule, however, may be fully justified in the analysis of minerals containing columbium and tantalum. See Chapter VI (4) (h).

##### (b) Preparation of the Standard Solution.

###### (\*) From Potassium Fluotitanate (according to Washington).

Potassium fluotitanate is most frequently used as the initial substance from which to prepare a standard solution of titanic sulfate.

It is easily purified by crystallization from hot water in a platinum vessel, and it does not contain enough alkali to interfere seriously with the gravimetric standardization of the solution. Since H. S. Washington<sup>7</sup> describes this method in considerable detail, his directions will be given here with but little modification. Concerning the preparation of pure potassium fluotitanate see p. 47.

As nearly as may be 1.5 grams of the anhydrous fluotitanate (equivalent to 1.61 grams of the hydrated salt,  $K_2TiF_6 \cdot H_2O$ ) is placed in a platinum dish, 5 grams of sulfuric acid (1:1) is added and the liquid is evaporated until fumes of sulfur trioxide have been escaping for some time and the residue is almost but not quite dry. Another 5 gram portion of the same acid is added and the evaporation repeated. These operations are gone through with four or five times. It is important that all hydrofluoric acid be expelled. The cooled residue is treated with 5 cc. of sulfuric acid (1:1), cold water is cautiously added, an additional 50 cc. of sulfuric acid (1:1) is introduced and the volume is made up with water to exactly 500 cc.

Washington<sup>8</sup> standardizes his solution by precipitating the titanium in a 50 cc. portion with ammonium hydroxide; but this seems unadvisable in the light of experiments by F. A. Gooch,<sup>9</sup> which go to show that when thrown out from an ammoniacal solution titanic acid is far more prone to occlude alkali than from one containing free acetic acid. Accordingly, the author prefers to employ the acetate method as described in Chapter VI (1) (f). It is also quite permissible to precipitate with cupferron—Chapter VI (1) (c).

Ten cc. of the standard solution is measured out with an accurate pipette into a 100 cc. volumetric flask, 5 cc. of hydrogen peroxide (3 per cent solution) is added and the remaining volume is made up with sulfuric acid (1:19). The peroxidized standard does not keep well; hence it is necessary to prepare it fresh for each batch of determinations.

(\*\*) **From Titanium Dioxide (according to Dunnington).**

Dunnington<sup>10</sup> prepares a reference solution of titanium sulfate in the following manner:

One gram of the purest obtainable titanic oxide is fused with a sufficient quantity of ammonium bisulfate (made by mixing together chemically equivalent quantities of ammonium sulfate and concentrated sulfuric acid) and the resulting mass is taken up with sulfuric acid (1:4). After filtering, if necessary, the volume is made up to 1000 cc. with the same acid.

The solution is standardized by evaporating a carefully measured portion to dryness in a tared platinum crucible and igniting the residue

to constant weight. Ammonium carbonate may be added to assist in vaporizing the last traces of sulfuric acid.

Five cc. of this solution is transferred to a 100 cc. graduated cylinder by means of a pipette, 20 cc. of sulfuric acid (1:4) and a sufficient excess of hydrogen peroxide are added and the volume is made up with water to the 100 cc. mark.

It may be remarked here that in case the standard solution is found to contain an appreciable quantity of iron, its amount should be determined, e.g., by the thiocyanate-colorimetric method,<sup>11</sup> and the proper deduction made. This correction would not be necessary, however, if the solution had been standardized by hydrolysis of the acetate in the presence of sulfurous acid.

### (c) The Test Solution.

The mode of preparing the test solution varies greatly according to the nature of the original material so that no general instructions can be given at this point. The matter will receive full consideration under the analysis of minerals and technical products.

### (d) Description of Various Colorimeters.

#### (\*) Dunnington's Colorimeter.

Dunnington has designed a simple and satisfactory form of colorimeter for use with Nessler tubes, which has been employed by him and his pupils for many titanium determinations, especially in soils.<sup>12</sup> It consists of a wooden box, as shown in Figure 16, with two horizontal partitions having holes to accommodate the several Nessler tubes A, B and C. From just below the lower partition board to the bottom the box is open on the front side; but contains the reflecting board R (end-view) which is set at an angle of about 45 degrees. The box is painted dull black on the inside, and the reflecting board is kept covered with a clean sheet of opaque white paper. It is of the greatest importance to select Nessler tubes of the same diameter; since, in using the instrument, it is assumed that the depth of the liquid is proportional to its volume. Unknown tubes may be readily tested by delivering water into them from the same pipette and observing whether or not the levels are equal.

In using the instrument it is placed in front of a window so as to be uniformly illuminated by diffuse daylight and free from shadows. The solution to be tested, whose volume need not be definitely known, is transferred to one of the comparison tubes, which in turn is placed in the colorimeter. The standard solution, prepared in the manner already

given (pp. 127-9), and which should be stronger than the test solution, is taken from the graduated cylinder G and introduced into one of the other tubes (side-view) by means of a pipette—the pipette being drained thoroughly after each delivery—until, when looked at from above, the liquids in the two tubes show no difference as to intensity of color. In case too much of the standard solution has been added, the excess is of course returned to the cylinder. The diminution in volume of the standard solution is now observed on the graduated cylinder; and, on the assumption that the two Nessler tubes contain equal quantities of titanium when the colors match, it is an easy matter to calculate

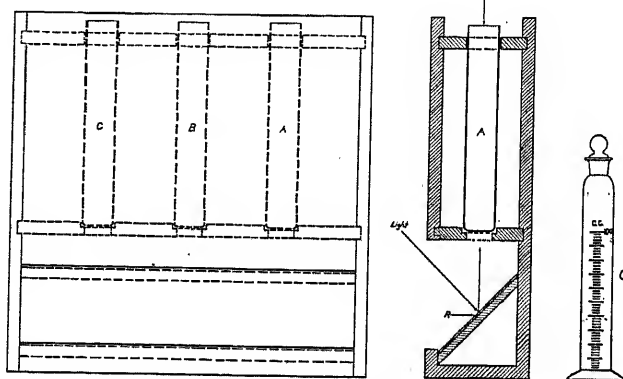


FIG. 16.—F. P. Dunnington's colorimeter.

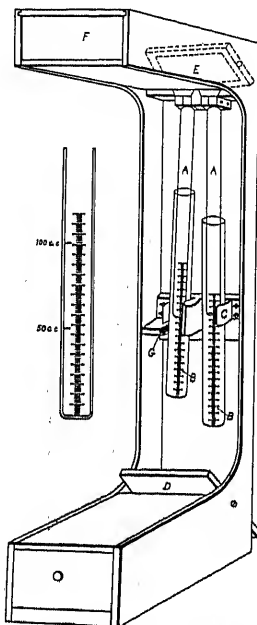
the amount of titanium in the unknown solution. Should the solution under examination afford a color deeper than the standard, it is made up to some convenient volume (say 100 cc.), and the amount of this diluted solution is determined that is required to match the standard.

(\*\*) **Schreiner's Colorimeter.**

O. Schreiner<sup>13</sup> has brought out a convenient colorimeter, which has given good service in connection with soil investigations carried on by the United States Department of Agriculture.<sup>14</sup> In this instrument (Figure 17) the comparison tubes are graduated on a linear basis, the smallest divisions being millimeters. The advantage of a linear graduation lies in the fact that the tubes are thus rendered independent of inequality of bore. Both the smaller immersion tubes A and the graduated comparison tubes B are ground and polished at the bottom. With the tubes held in position by means of the clamps C and containing suitable quantities of the solutions to be compared, light is thrown upwards through the tubes by the reflector D (covered with white paper

or milk glass), and with the mirror E set at the proper angle two circular images reach the eye of the observer at F, which will be more or less intensely colored according as the tubes B are lowered or raised, the positions of the plungers A being fixed.

In making a determination then the standard solution, prepared as described on p. 127, is poured into one of the comparison tubes, which is put into place in the camera. In like manner, the solution to be tested, having been brought to a definite volume, which should be so



(*Journal of the American Chemical Society*, vol. 27, p. 1192, 1905.)

FIG. 17.—O. Schreiner's colorimeter.

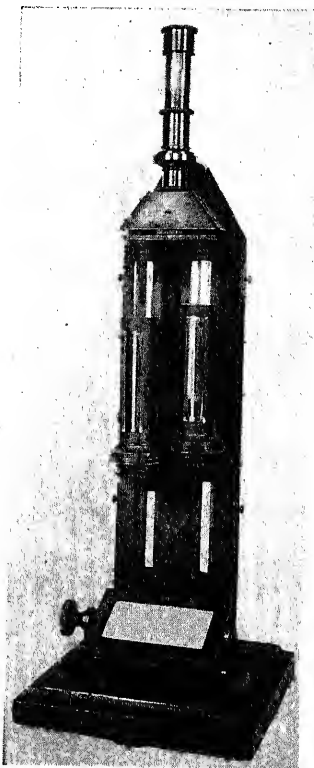
chosen that the concentration of the unknown solution is somewhere near that of the standard, is introduced into the other tube, which is placed in juxtaposition to the standard. The tube containing the test solution is now set at some convenient height, e.g., the 40 mm. mark, and the other tube containing the standard solution is moved up or down until there is no distinction as to color. It is well to make two settings, first by going from a stronger to a weaker shade and then from a weaker to a stronger, and average the two readings. It is now obvious that the heights of the two columns of liquid, measured from the bottom of the plunger to the bottom of the tube, are to each other inversely



as the concentrations of the two solutions. In other words, if  $R$  is the reading of the standard of strength  $S$  and  $r$  the reading of the test of unknown strength  $s$ , then

$$s = RS/r$$

With this instrument standard glass slides, such as those of J. W. Lovibond,<sup>15</sup> may be substituted for the standard solution, the slide being inserted in the slot  $G$  below the immersion tube.



(Manufactured by E. Leitz, Inc., New York City.)

FIG. 18.—Duboscq-Leitz colorimeter.

It is also interesting to note that, because peroxidized titanium solutions do not keep, A. Gautier<sup>16</sup> has proposed the use of an aqueous solution of methyl orange as a permanent standard. Since the methyl orange solution must be standardized against titanium, this mode of procedure would be admittedly less exact.

(\*\*\*) The Duboscq-Leitz Colorimeter.

Various modifications of Duboscq's dipping colorimeter have been placed on the market. One of these, the Duboscq-Leitz<sup>17</sup> colorimeter, is shown in Figure 18. This instrument is similar in principle to Schreiner's colorimeter; but by means of suitable optical attachments the operator observes a circular image divided by a diametral line, the color intensities of the two halves corresponding to the standard and test solutions respectively. Moreover the plungers are of solid glass and the bottoms of the comparison jars are glass disks with plane surfaces sealed on by cement, thus rendering the image perfectly bright and free from distortion.

This type of colorimeter is probably capable of yielding more accurate results than the simpler forms; but it is much more expensive, and is open to the objection that sooner or later the corrosive liquids loosen the cement and cause trouble.

(\*\*\*\*) Other Colorimeters.

Both J. W. Mellor<sup>18</sup> and W. F. Hillebrand<sup>19</sup> describe modifications of Weller's original colorimeter. In this type the comparison jars are of square or rectangular cross-section and are viewed laterally by transmitted light. The standard, which should be stronger than the test, is diluted with a measured volume of water until the two solutions show the same concentration with respect to titanium. Furthermore, Washington<sup>20</sup> gives directions whereby any chemist may construct a camera for use with square glasses from materials of trifling cost.

There are other colorimeters, which are to be found described and illustrated in various works on analysis<sup>21</sup> and also depicted in the catalogues and circulars of apparatus venders.

(e) Interfering Substances.

(\*) Substances Imparting Color to the Test Solution.

Although it is quite feasible to compare colors of the same kind as to their relative intensities, it is extremely difficult to do so when there is a marked difference in the quality of the color; hence due regard must be paid to the possible presence of those elements which impart color by virtue of their own ions, either before or after the peroxidation of the test solution.

As already mentioned (p. 61), chromium, vanadium and molybdenum give conspicuous colors with hydrogen peroxide. These substances may all be removed by fusing the sample with sodium carbonate and a little sodium nitrate and leaching the melt with water, the residue being brought into sulfuric acid solution.

Uranium, should it ever be present, would interfere because of the rather high tinctorial power of its compounds. Titanium may be separated from uranium in accordance with methods given in Chapter VI (4) (1).

Iron, the omnipresent component of titaniferous materials, owing to the pale brownish yellow color of ferric sulfate tends to cause slight errors of excess in the colorimetric estimation of titanium. If so desired, iron may be removed by any of the methods given above—Chapter VI (4) (a); but such a course would hardly be justified for two reasons. In the first place, the error from this source alone is not likely to be of great moment. According to Hillebrand's<sup>22</sup> statement, which is based on experimental evidence, the coloring effect of 0.1 gram of ferric oxide in 100 cc. of a solution containing 5 per cent of sulfuric acid by volume is about equal to 0.0002 gram of titanous oxide in the same volume similarly acidified when oxidized by hydrogen peroxide. Supposing then that a 1 gram sample of the original substance had been taken for analysis and that it contained 10 per cent of ferric oxide, the result for titanium oxide would be vitiated to the extent of only 0.02 per cent. Moreover, the error produced by ferric sulfate is somewhat offset by the bleaching effect of alkali salts (see below), which so often remain in the solution as the result of fusions to aid in dissolving the material. In the second place, the influence of ferric sulfate may be corrected for by any of the following methods with much less expenditure of time and labor than by an actual separation.

First: having determined the iron in a separate experiment, the apparent titanium value may be corrected according to Hillebrand's rule (see above).

Second: an equal quantity of iron may be added to the standard by means of a solution of ferric sulfate of known strength, as proposed by W. A. Noyes.<sup>23</sup> This expedient could not be employed with either the Schreiner or Duboscq colorimeter, though it is practicable with Nessler tubes (Dunnington's colorimeter). With the unknown solution in one tube, the requisite amount of ferric sulfate and usual excess of hydrogen peroxide are introduced into the other. Sulfuric acid (1:19) is then added until the volume is approximately equal to that of the test. The undiluted standard (p. 127) is now dropped in from a burette, a little at a time with stirring, until the two liquids appear to be identical in color. For methods of adding iron when Weller's form of colorimeter is being used consult Hillebrand.<sup>24</sup>

Third: the test solution may be practically decolorized by phosphoric acid as far as ferric sulfate is concerned; but, since phosphoric acid also exerts a bleaching action on pertitanic salts, an equal quantity must be added to the standard solution as well. J. H. Walton, Jr.<sup>25</sup> and

Faber <sup>26</sup> have both experimented with this method and obtained satisfactory results. Having determined the amount of phosphoric acid necessary to decolorize the test solution by actual trial, its addition to the standard solution is carried out by the same methods as in the case of ferric sulfate (see above).

(\*\*) **Substances Exerting a Bleaching Action on the Test Solution.**

Hillebrand <sup>27</sup> has called attention to the deleterious action of hydrogen fluoride in the colorimetric estimation of titanium. Hydrofluoric acid and fluosilicic acid have both been detected as impurities in commercial hydrogen peroxide. It is therefore important to use a reagent that is known to be entirely free from fluorine compounds; and, in case hydrofluoric acid or alkali fluorides have been used in the preliminary decomposition of the sample, the complete expulsion of fluorine cannot be too strongly emphasized.

The bleaching effect of phosphoric acid has already been noted; hence in the analysis of phosphatic materials its amount may occasionally be large enough to necessitate a correction.

H. E. Merwin <sup>28</sup> has made the observation that alkali salts weaken the color of peroxidized titanium solutions to a noticeable extent. This bleaching effect increases with the concentration and alkali sulfate and decreases with concentration of free sulfuric acid. Furthermore, the color of solutions thus bleached is intensified both by increase of temperature and by addition of acid. However, the error produced by alkali sulfates in ordinary analytical practice is not likely to be very great. Concerning its magnitude in rock analysis Merwin writes as follows: "In rock analysis by using 6 grams of pyrosulfate, which is equivalent to 4 grams of normal sulfate and 2 grams of acid, for the melt containing the titanium, and dissolving this in water to which 10 cc. of strong sulfuric acid has been added, a nearly negligible correction of only 3 per cent need be added. If the titanium dioxide exceeds 0.02 gram no correction is required. In case the melt is dissolved in 100 cc. of 5 per cent sulfuric acid, the titanium found—if the amount is between 0.002 gram and 0.01 gram—is too low by approximately 0.0004 gram".

**(f) Accuracy of the Hydrogen Peroxide Method.**

R. C. Wells <sup>29</sup> has studied the sensitiveness of the hydrogen peroxide test for titanium and has come to the conclusion that normally the error should not exceed 2 parts in 100 throughout a wide range of concentrations.

## (2) THE DETERMINATION OF TITANIUM WITH THYMOL.

V. Lenher and W. G. Crawford<sup>30</sup> have based a colorimetric method for titanium on the deep red color formed between titanous sulfate and thymol in strong sulfuric acid. For the maximum development of color the resulting solution should contain at least 79.4 per cent (sp. gr., 1.725), and not less than 0.006 gram of thymol should be added for every 0.0001 gram of titanous oxide. The color diminishes with rise of temperature; but, up to 90°C., it returns to its original value on cooling to room temperature (20°C.). At 100°C. and higher a portion of the color is permanently destroyed. The intensity of the coloration is claimed to be at least twenty-five times as great as that produced by hydrogen peroxide. Hydrofluoric acid bleaches the color while tungstic acid causes an apparent increase. Chlorides, phosphates and tin are without effect.

The reagent is best prepared by dissolving thymol in a little glacial acetic acid and adding concentrated sulfuric acid thereto until the requisite volume has been reached. The reagent keeps fairly well in the absence of bright light.

In making a determination, the titanium-bearing substance is fused with potassium pyrosulfate, the melt taken up in concentrated sulfuric acid and the thymol reagent added at once—the comparison being made in any convenient form of colorimeter.

The test analyses of Lenher and Crawford are very satisfactory, some of the results being in good agreement with those obtained by Weller's method; but it does not appear that this mode of procedure has many advantages over the hydrogen peroxide process in general use. The necessity for working with strong sulfuric acid media instead of dilute aqueous solutions is an objection of a practical nature. Furthermore, the analyst need scarcely bother himself about quantities of titanium too small to be estimated by the hydrogen peroxide method.

## (3) THE DETERMINATION OF TITANIUM WITH SALICYLIC ACID.

On account of the strong yellow color formed between salicylic acid and a titanium salt in nearly neutral solution, J. H. Muller<sup>31</sup> has suggested the use of this substance as a colorimetric reagent for titanium. The standard solution is prepared by fusing a weighed quantity of pure titanium dioxide with potassium carbonate, disintegrating the melt with warm water and then adding salicylic acid in some excess. By similar treatment a small unattacked residue is likewise brought into solution. Presumably the test solution is gotten by a similar technique, after prior removal of interfering substances. Increase in the concentration of potassium salicylate does not seem to affect the intensity

of color, and the same is true of salicylic acid. When, however, very small amounts of titanium are under consideration, the color fades unless a sufficient excess of salicylic acid be added. Hydrofluoric acid exerts its usual bleaching action, mere traces of iron in the ferric condition interfere by imparting the characteristic purple color<sup>32</sup> and molybdenum (alkali molybdate) gives rise to a very similar yellow color. Finally, the influence of certain other elements (zirconium, thorium, rare earths, columbium and tantalum), some of which are not without action, is discussed in the original paper.

(4) THE DETERMINATION OF TITANIUM AND VANADIUM IN THE PRESENCE OF EACH OTHER.

Vanadium gives with hydrogen peroxide, under conditions similar to those employed in testing for titanium, a reddish brown color owing to the formation of pervanadic acid. J. A. Fenner<sup>33</sup> makes use of this reaction for the colorimetric estimation of vanadium in the presence of titanium by adding enough hydrofluoric acid to destroy the color of the latter, the former being unaffected. In like manner, A. W. Gregory<sup>34</sup> utilizes the reaction between vanadic acid and strychnine in a strong sulfuric acid medium, allowing the solution to stand until the transient violet color gives place to orange—titanium being apparently unaffected. On the other hand, H. J. H. Fenton<sup>35</sup> has shown that the color produced by dihydroxymaleic acid<sup>36</sup> in titanium solutions, which varies from orange-red to straw-yellow depending upon the dilution, is independent of vanadium.

By using both Fenton's acid and hydrogen peroxide Mellor<sup>37</sup> has worked out an ingenious method for the simultaneous determination of small quantities of titanium and vanadium in the colorimetric way. Dilute sulfuric acid solutions of titanium and of vanadium are peroxidized and measured in Lovibond's tintometer<sup>38</sup> (using 1 inch trough), and the results with the red rays are plotted on coordinate paper, letting the abscissas represent values on Lovibond's scale and the ordinates concentrations of titanium and vanadium respectively. In like manner, titanium solutions are treated with Fenton's reagent and the observations similarly charted. In this way three straight-line curves are obtained, which may be expressed by the following equations:

- (1) Titanium (Fenton's acid)  $y = 151.2x$
- (2) Titanium ( $H_2O_2$ )  $y_1 = 39.03x_1$
- (3) Vanadium ( $H_2O_2$ )  $y_2 = 52x_2$

in which  $y$ ,  $y_1$ , and  $y_2$  denote the intensity of the red ray on Lovibond's scale and  $x$ ,  $x_1$ , and  $x_2$  the amount of titanium dioxide or vanadium pentoxide expressed in grams per liter of solution.

Having determined the amount of titanium through the agency of Fenton's compound, the corresponding value of the red ray on Lovibond's scale can be computed for the peroxide coloration either from the graph or from the equation of the curve (equation 2). Since the intensity of the red ray for the mixture of titanium and vanadium can be determined experimentally in another aliquot part of the test solution, the effect due to titanium can be deducted, and the remainder will represent the intensity of the red tint produced by vanadium. The amount of vanadium can then be calculated either graphically or from equation (3).

In commenting upon this process, Hillebrand <sup>39</sup> says: "The method requires great care and is vitiated by the presence of more than traces of iron". Mellor <sup>40</sup> recommends that the iron be removed either by precipitation as ferrous sulfide in the presence of ammonium tartrate (p. 96) or by extraction of the hydrochloric acid solution with ether (p. 101).

## Chapter VIII.

### Oxidimetric Methods.

#### (1) PRELIMINARY REMARKS.

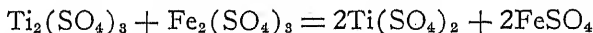
All of the earlier attempts to determine titanium oxidimetrically led to somewhat erroneous results (lower than the true values) owing either to incomplete reduction of the titanium to the trivalent state or to inadequate protection of the deoxidized solution against atmospheric oxidation.<sup>1</sup> More recent work, however, especially that of G. E. F. Lundell and H. B. Knowles,<sup>2</sup> has clearly demonstrated that by means of a comparatively simple mechanism the volumetric estimation of titanium can be quickly and accurately performed.

#### (2) THE DETERMINATION OF TITANIUM BY TITRATION WITH POTASSIUM PERMANGANATE OR POTASSIUM DICHROMATE.

##### (a) Reduction in a Flask.

F. Pisani<sup>3</sup> was the first to propose the quantitative determination of titanium by reduction of a titanic to a titanous salt through the agency of zinc and acid and its subsequent titration with potassium permanganate. C. Marignac<sup>4</sup> endeavored to improve Pisani's process, but obtained low results. H. L. Wells and W. L. Mitchell,<sup>5</sup> in taking the matter up, used carbon dioxide to protect the solution; but in spite of this precaution their test analyses show decided errors of loss (hydrated potassium fluotitanate being taken as the reference substance).

In contrast to the above, H. D. Newton<sup>6</sup> has worked out a very successful process for the estimation of titanium, which depends upon reduction with zinc in an atmosphere of hydrogen, addition of ferric sulfate solution in excess and titration of the resulting and equivalent ferrous salt with potassium permanganate—the reaction between the salts of titanium and iron taking place in accordance with the following equation:



The sulfuric acid solution of titanium is introduced into a small flask (100 cc.) and water or acid is added until at the final volume there



is present about 10 per cent of concentrated sulfuric acid. A weighed quantity of granular zinc<sup>7</sup> of known iron content is then added, and the flask is closed with a two-hole rubber stopper fitted with a delivery tube and a small separatory funnel. After the air has been driven out of the flask by the escaping hydrogen, the exit tube is dipped into water and the stopcock of the funnel is closed. The reaction is hastened by the moderate application of heat until the zinc has completely dissolved; whereupon the solution is cooled and a liberal excess of ferric sulfate is run in from the tap funnel, followed at once by cold water (freshly distilled) in sufficient amount to fill the flask to its neck. Since the oxidation of a sulfuric acid solution of ferrous sulfate on exposure to the air at ordinary temperatures is a very slow process,<sup>8</sup> the flask may now be opened with impunity and its contents transferred to a larger vessel containing some more cold water. The titration is made with a standard solution of potassium permanganate in the usual manner, it being of course necessary to correct the titer for the small amount of iron in the zinc used to effect reduction.

Newton experimented with from 0.05 gram to 0.16 gram of titanium dioxide and obtained excellent results. The method was employed by J. Brown<sup>9</sup> for determining titanium in zircon and baddeleyite—the values being in very satisfactory agreement with those gotten gravimetrically.

Wells<sup>10</sup> modifies Newton's procedure by using a one-hole stopper supplied with an exit tube bent twice at right angles to close the flask, thus omitting the separatory funnel. The end of the tube is placed near the bottom of a beaker containing ferric sulfate solution. When the zinc has dissolved, diminution of pressure with cooling causes the ferric sulfate to recede into the flask. This simplified technique seems to yield accurate results.<sup>11</sup> Finally, A. Gemmell<sup>12</sup> uses an alloy composed of 90 per cent zinc and 10 per cent aluminum for the reduction, and also introduces certain innovations in the manipulation as compared with Newton's original method.

### (b) Reduction in the Zinc or Cadmium Reductor.

Contrary to statements made by P. W. and E. B. Shimer<sup>13</sup> and C. Van Brunt<sup>14</sup> to the effect that amounts of titanium ordinarily handled when operating on the analytical scale are not completely reduced by passage through the reductor of C. Jones,<sup>15</sup> W. F. Hillebrand<sup>16</sup> reports a procedure of J. A. Holladay, wherein a reductor tube of the usual dimensions is prescribed. Lundell and Knowles<sup>17</sup> have made a careful study of the situation, and have found that as much as 0.11 gram of titanium may be quantitatively reduced by means of a reductor having

a bore of 1.9 cm. and a column of amalgamated zinc 43 cm. long. The solution should contain 3-5 per cent of concentrated sulfuric acid by volume, but it need not be heated hotter than 25°C. It is necessary to deliver the deoxidized titanium solution well below the surface of a solution of ferric sulfate of sufficient strength to present a three to five-fold excess of the fixing agent; for otherwise the sensitive titanous sulfate will suffer serious oxidation by exposure to air. When these precautions are taken, highly accurate results may be confidently expected.

### (\*) Preparation of Reagents

*Potassium Permanganate.* A 0.1 N solution of potassium permanganate would contain 3.161 grams of the salt in every liter; but, since in practice it is not worth while to attempt the adjustment of a solution to the exact preconceived normality, it suffices to dissolve about 3.2 grams of the crystals (as free from chlorine compounds as may be) in 1000 cc. of water. This solution gradually changes strength owing to the slow oxidation of the traces of organic matter ordinarily present in distilled water at the expense of the permanganate; hence it should be allowed to stand 8-14 days prior to use.<sup>18</sup> At the end of this time it is filtered through an ignited felt of asbestos in such a way as not to allow the clear liquid to come into contact with any of the rubber connections. The two inch perforated platinum cone (Figure 23) of F. A. Gooch<sup>19</sup> may be used with advantage in the present case; since it permits rapid filtration with no sacrifice as to clarity. The oxidation of the organic matter, however, may be greatly hastened by simply boiling the solution vigorously for about 10 minutes; but it should be cooled thoroughly before filtering. The solution should be kept in a glass stoppered bottle and protected from reducing vapors and dust as much as possible by placing an inverted beaker (without lip) over the stopper, and except during actual use it is well to keep the bottle in a dark cupboard. Under these conditions a solution will not noticeably change its standard throughout a period of 60 days. Moreover, according to the experience of W. Blum,<sup>20</sup> the addition of 1 per cent of potassium hydroxide greatly retards the decomposition of permanganate solutions.

Sodium oxalate, which may be obtained from the Bureau of Standards of certified purity, is undoubtedly the best substance against which to standardize potassium permanganate solutions.<sup>21</sup> The oxalate is dried at a temperature not lower than 105°C. and not higher than 240°C. and preserved in a desiccator. It is employed in accordance with the technique of R. S. McBride.<sup>22</sup> In a 400 cc. beaker 0.25 to 0.30 gram of the sodium oxalate is dissolved in 200 to 250 cc. of hot

water (80-90°C.) and the solution is acidified with 10 cc. of sulfuric acid (1:1). The titration is made at once with the 0.1 N potassium permanganate, *stirring the liquid vigorously and continuously*. The permanganate must not be run in more rapidly than 10 to 15 cc. per minute, and the last 0.5 to 1 cc. must be added drop by drop, with special care to allow each drop to be fully decolorized before the next is introduced. The small excess of permanganate required to produce an end-point should be estimated by matching the color in another beaker of the same size containing the same bulk of acid and hot water.<sup>23</sup> The temperature of the solution should not be lower than 60°C. at the time the end-point is reached. In the standardization of more dilute permanganate solutions the initial volume should be proportionately smaller; e.g., with 0.03 N permanganate 75 cc. of water and 4 cc. of sulfuric acid (1:1) should be used.

*Ferric Sulfate (Ferric Ammonium Sulfate)*. D. L. Randall<sup>24</sup> has employed a solution of iron alum (100 grams of the salt per liter of water) for registering the reduction of molybdenum; but Lundell and Knowles<sup>25</sup> prefer the simple ferric sulfate, which they prepare in the following way:

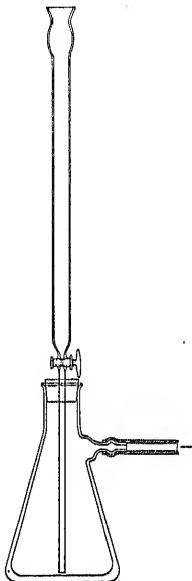
Twenty grams of ingot iron or plain carbon steel<sup>26</sup> is dissolved in a slight excess of hydrochloric acid, and the resulting solution is oxidized with nitric acid; whereupon 80 cc. of concentrated sulfuric acid is added, and the whole is evaporated down until fumes of sulfur trioxide are freely evolved. After cooling, water is added till the volume equals 1000 cc., the vessel is placed on the steam bath until all sulfate has dissolved and the clear solution is treated with 0.1 N potassium permanganate in sufficient quantity to impart a faint pink color to the liquid which persists for 5 minutes.

### (\*\*) Charging the Reductor

A. A. Blair's<sup>27</sup> method for amalgamating the zinc is as follows: Five grams of mercury is dissolved in 50 cc. of nitric acid (1:1) and the solution so obtained is diluted to 250 cc. This is transferred to a liter flask, and 500 grams of granulated zinc, which passes a 20-mesh but stands on a 30-mesh sieve, is introduced. The mixture is shaken vigorously for a minute or two, after which the liquid is poured off and the zinc is thoroughly washed by decantation with distilled water. The material is then dried and preserved in a glass bottle for future use.

The reductor (Figure 19) is first choked with a few glass beads. On top of this a plug of glass wool (about 8 mm. thick) is placed, and asbestos emulsion is poured in while gentle suction is being applied until a layer of about 1 mm. is obtained. The tube is then filled with

the amalgamated zinc until a column of the requisite length (p. 141) has been formed. It is well also to place a little glass wool on top of the zinc to serve as a filter.



(*Transactions of the American Institute of Mining Engineers*, vol. 17, p. 414, 1889.)

FIG. 19.—C. Jones' reductor.

#### (\*\*\*) Performance of the Analytical Process

The reductor is first washed out with dilute sulfuric acid (5 per cent by volume)—leaving enough liquid in the tube, however, to completely cover the zinc. The receiving flask is then emptied of the preliminary washings and charged with a three to five-fold excess of the ferric sulfate solution.<sup>28</sup> There are then added in order the following solutions: 25-50 cc. of dilute sulfuric acid (3-5 per cent by volume), the titanium solution, which should have the same acidity and occupy a volume of about 150 cc., 100 cc. more of the dilute acid and finally 100 cc. of water. Each solution is introduced at the room temperature (25°C. or higher) and drawn through at a speed of approximately 100 cc. per minute—at no time allowing the zinc column to become exposed to air. The suction is gradually released, the exit tube is rinsed both inside and out and with the receiver placed under the burette the deoxidized solution is titrated at once with 0.1 N potassium permanganate. A blank experiment should always be made, using the

same quantities of reagents and introducing them into the reductor in exactly the same manner, and the small titer thus obtained (corresponding to impurities in the zinc) subtracted from the main titer in order to arrive at the true amount of titanium.<sup>29</sup>

#### (\*\*\*\*) Interfering Substances

The presence of any substance that would yield under the reducing conditions a compound (or compounds) reactive toward permanganate would of course vitiate the results for titanium. The most important of these are: certain organic compounds, nitric acid, tin, arsenic, antimony, molybdenum (III), iron (II), chromium (II), vanadium (II), tungsten, uranium and columbium.<sup>30</sup> The effect of the first five is indefinite and varies according to circumstances. Molybdenum, iron, chromium and vanadium are quantitatively reduced to the indicated valences. Tungsten, uranium and columbium do not undergo definite changes of valence. Tungsten approaches the quinquivalent state and columbium the trivalent; while uranium is reduced somewhat below the quadrivalent condition, i.e., a mixture of quadrivalent and trivalent uranium is obtained.<sup>31</sup> Organic matter and nitric acid may be removed during the preliminary treatment of the sample according to well known methods. Tin, arsenic, antimony and molybdenum may all be precipitated by hydrogen sulfide in acid solution. Iron may be separated from titanium, preferably by the sulfide process—Chapter VI(4) (a) (\*), or determined volumetrically by any one of several procedures that are independent of titanium (see below). Chromium, vanadium, tungsten and uranium may be separated from titanium by treating a solution made alkaline with sodium carbonate with sodium peroxide and boiling until sodium pertitanate has been completely decomposed—titanic acid remaining undissolved (cf. p. 110). Furthermore, according to statements by Van Brunt,<sup>32</sup> titanium, iron and chromium in admixture may all be determined by volumetric processes (see below). Columbium, not being a commonly occurring element, is seldom met with in the analysis of titaniferous materials—a fact to be appreciated by the analyst; since methods for differentiating columbium and titanium leave much to be desired—cf. Chapter VI(4) (h).

#### (\*\*\*\*\*) The Cadmium Reductor.

W. D. Treadwell<sup>33</sup> has shown that a comparatively thin layer of cadmium in fine particles and not amalgamated will serve many of the purposes that are ordinarily accomplished by means of the much longer column of amalgamated zinc. The cadmium is prepared by electrolysis of a solution of cadmium sulfate acidified with sulfuric acid, using a current of 30 amp. per sq. dm. A solution of titanic sulfate is com-

pletely reduced on being passed through the reductor tube, which is charged with cadmium powder to a depth of only 5 to 7 cm., and the resulting titanous sulfate is titrated electrometrically. For further details the original article should be consulted.

### (c) Reduction with Liquid Amalgams in a Separatory Funnel.

T. Nakazono<sup>34</sup> and several other Japanese chemists<sup>35</sup> have developed a number of volumetric processes which depend upon the deoxidation of the solution under examination by shaking with liquid amalgam in a separatory funnel of special construction.<sup>36</sup> The amalgam is prepared by dissolving 3-4 grams of zinc in 100 grams of mercury. A similar amalgam containing cadmium was used in some of the work. Titanic sulfate in solution of regulated acidity, when shaken with the amalgam in an atmosphere of carbon dioxide, is completely reduced to titanous sulfate, which after removal of the amalgam may be titrated in the funnel with potassium permanganate without allowing any air to enter. The amalgam may be used repeatedly, and the customary blank run is usually not necessary.

## (3) THE DETERMINATION OF TITANIUM BY TITRATION WITH A FERRIC SALT.

### (a) Reduction in a Flask or Separatory Funnel.

E. Knecht and E. Hibbert<sup>37</sup> were the first to employ a standard solution of ferric salt for the titrimetric estimation of titanium. They reduced the titanous salt with zinc and hydrochloric acid in a flask fitted with a Bunsen valve, and titrated with a standard solution of ferric chloride while a stream of carbon dioxide was being introduced into the flask—the end-point being ascertained by means of potassium thiocyanate used as outside indicator. According to more recent communications<sup>38</sup> this procedure has been considerably modified. The thiocyanate is added directly to the test solution—thus avoiding the inconvenient “spot testing”, iron alum is substituted for ferric chloride in the standard solution and the reduction flask of Hibbert (Figure 20) is recommended for the purpose, the exact manner of using which will be given under (4).

G. Gallo<sup>39</sup> and F. W. Hinrichsen<sup>40</sup> have brought forward very similar processes, the latter advocating a zinc-magnesium alloy (containing 50 per cent of each metal) as reducing agent.

T. R. Ball and G. McP. Smith,<sup>41</sup> in order to avoid waiting for the last of the zinc to dissolve, carry out the reduction in a 250 cc. separatory funnel, the stem of which is attached to another tube containing

a filter of asbestos on glass wool. Having filled the stem of the funnel with freshly boiled water, the titanium solution along with a liberal amount of zinc is introduced into the bulb and 10 cc. of either concentrated hydrochloric acid or sulfuric acid (1:1) is added. All air is expelled from within the system by a current of carbon dioxide, and the mouth of the funnel is closed with a modified Contat-Göckel valve,<sup>42</sup> which too should be filled with carbon dioxide. The reduction is allowed to proceed for about 2 hours at the ordinary temperature; whereupon the valve is removed and the solution drawn through the filter into a suction flask previously filled with carbon dioxide, the funnel being washed with air-free water without permitting air to enter the funnel tube. The deoxidized solution is now rapidly titrated with a standard solution of ferric chloride, using 1 cc. of potassium thiocyanate (saturated solution) as indicator.

The test analyses of Ball and Smith, which were made on from 0.002 to 0.06 gram of titanium dioxide, are very satisfactory. Like all methods that involve titrating with a ferric salt, the process is quite independent of iron in the original material; but tin, chromium, vanadium, tungsten, molybdenum and perhaps other substances must be absent.

A. M. Morley and J. K. Wood<sup>43</sup> reduce with aluminum foil in a partially closed flask, cool in an atmosphere of carbon dioxide and titrate with a current of the protective gas passing into the flask. They employ a solution very strongly acidified with hydrochloric acid, and claim that under such conditions a rapid reduction ensues. They also titrate the iron alum solution against a known quantity of titanium, following the same procedure—thus taking advantage of an empirical standardization. The titer is subject to a small correction, varying with the amount of aluminum used, which is determined by means of a blank estimation. The results show an accuracy greater than 1 part in 100.

#### (b) Reduction in the Zinc Reductor.

Shimer and Shimer,<sup>44</sup> in order to ensure complete reduction of the titanium, employ a very long reductor tube (0.95 cm. by 91 cm.), which is charged with amalgamated zinc of somewhat coarser grain than is usually prescribed, i.e., 10 to 20-mesh instead of 20 to 30-mesh. L. E. Barton<sup>45</sup> secures a large surface of contact by using a shorter but wider tube,<sup>46</sup> viz., 3.8 cm. by 38 cm. Both the Shimers and Barton operate with hot solutions. Since, however, the more recent experiments of Lundell and Knowles (p. 140) have proven that a reductor of abnormal shape or size is not required and that cool solutions are preferable to hot,<sup>47</sup> it does not seem necessary to give here any special

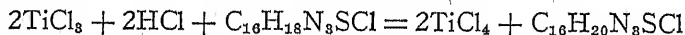
technique for the use of either the extra-long or extra-wide reductor. Suffice it to say then that the deoxidized solution is caught in a flask kept full of carbon dioxide, and after disconnecting is titrated as promptly as may be with a standard solution of ferric ammonium sulfate, using 5 cc. of a saturated solution of potassium thiocyanate as indicator, until a drop of the reagent imparts a brownish color to the liquid that remains for at least 1 minute.

The ferric ammonium sulfate solution, if free from ferrous iron, may be conveniently standardized by putting it through the reductor and titrating with potassium permanganate solution which has been previously tested against sodium oxalate. The technique given above (p. 143) applies equally well to iron solutions.

In the opinion of E. F. Hickson and other Bureau of Standards analysts<sup>48</sup> the method has a tendency to give results that are a little too low. On the other hand, it has the advantage over the permanganate titration in that titanium may be determined in the presence of large amounts of iron, thus avoiding the estimation of the latter by means of a separate experiment in order to arrive at the true value for titanium (cf. p. 146).

#### (4) THE DETERMINATION OF TITANIUM BY TITRATION WITH METHYLENE BLUE.

The use of a standard solution of methylene blue for the volumetric estimation of titanium was first brought out by Hibbert,<sup>49</sup> though the same reaction had been previously utilized by Knecht<sup>50</sup> for the quantitative determination of methylene blue. In the presence of hydrochloric acid titanous chloride reduces this dyestuff definitely to methylene white in accordance with the following equation:

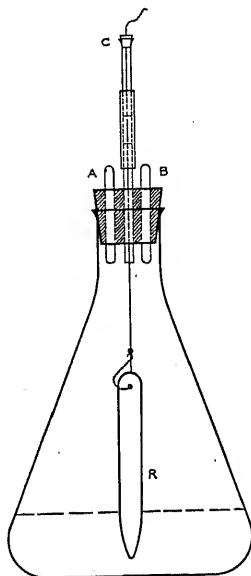


The solution of titanous chloride along with a sufficient quantity of hydrochloric acid is introduced into a flask fitted with a three-hole rubber stopper; one of these is supplied with a Bunsen valve, through which a platinum wire having a stick of zinc attached to it is passed, and the other two holes are temporarily closed with short pieces of glass rod (see Figure 20). The zinc is thus immersed in the titanium solution, and when the action has gone on for 15 to 20 minutes and the liquid has been boiled, one of the rods A is removed, and carbon dioxide is passed into the flask through a tube inserted in its place. The zinc is then lifted free of the liquid by drawing the platinum wire upwards through the small pierced rubber stopper C. The other glass rod is then removed also, and the zinc is washed with a little freshly



boiled water by inserting the wash bottle tip through the hole previously occupied by the rod B; whereupon the solution is titrated while warm (about 35°C.) with standard methylene blue, the burette tip being placed in the opening at B, until a permanent blue tint is obtained.

The standard solution of methylene blue is prepared by dissolving the medicinal compound in water, using 4.67 grams or 9.34 grams for every liter according as a 0.025 N or 0.05 N solution is desired. The standardization is accomplished by titrating a measured portion acidi-



(*Journal of the Society of Chemical Industry*, vol. 28, p. 189, 1909.)

FIG. 20.—Eva Hibbert's reduction flask.

fied with hydrochloric acid with titanous chloride which has in turn been standardized against a known quantity of ferric iron;<sup>51</sup> or, if preferred, against pure potassium chlorate in the manner proposed by F. W. Attack.<sup>52</sup>

Hibbert experimented with from 0.00158 to 0.03867 gram of titanium and obtained very good results, even in the presence of a considerable quantity of iron.

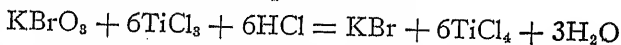
B. Neumann and R. K. Murphy<sup>53</sup> have made a somewhat detailed study of this process; and, while reporting favorably upon it, they advocate a somewhat modified procedure. Murphy's<sup>54</sup> directions are as follows: The hydrochloric acid solution of the material to be analyzed, which must be free from both nitric and sulfuric acids, is treated

with an additional quantity of acid (about 30 cc. of concentrated hydrochloric acid), some 2 grams of zinc dust and a few pieces of zinc are added and the reduction is allowed to proceed for 15 to 20 minutes in a covered beaker. When most of the zinc has dissolved, the solution is filtered as quickly as possible into an Erlenmeyer flask through which a current of carbon dioxide is maintained. Twenty cc. of concentrated hydrochloric acid is added and the reduction is completed by immersing a stick of zinc in the liquid for a few minutes and then heating very nearly to the boiling point. The apparatus is essentially the same as that of Hibbert, the chief difference being that the third hole in the stopper is dispensed with.<sup>55</sup> With the solution now occupying a volume of about 150 cc. and while carbon dioxide is passing, the zinc is removed from the solution and the titanous chloride titrated with methylene blue, the burette tip being inserted through the slit in the Bunsen valve.

In case nitric or sulfuric acid has been used in the preliminary treatment, either may be eliminated by precipitating with ammonium hydroxide, washing the precipitate with water and redissolving in warm hydrochloric acid. Ferrous chloride does not react with methylene blue; hence the method is applicable to ferruginous materials without reserve. Tin, vanadium, tungsten, molybdenum and sulfurous acid interfere and must therefore be absent.

#### (5) THE DETERMINATION OF TITANIUM IODOMETRICALLY WITH THE AID OF POTASSIUM BROMATE.

W. Boller <sup>56</sup> has proposed the use of potassium bromate as an oxidizing agent for the valuation of commercial specimens of titanous chloride. When the latter salt is added to an excess of this reagent, the fundamental reaction may be expressed thus:



A measured portion of the titanous salt solution is added to an accurately known quantity of the bromate in a flask with special attachments,<sup>57</sup> the interior of which has been deprived of air. A sufficient quantity of hydrochloric acid is assumed to be present in the titanous chloride: if not, more may be added. The amount of oxidizer left over is then estimated by introducing potassium iodide in excess, opening the flask and titrating the liberated iodine with a standard solution of sodium thiosulfate, using starch emulsion as indicator.

The process is claimed to be independent of the small amounts of iron that are usually present in technically prepared titanium trichloride; since, though oxidized to ferric salt at the expense of the bromate, it is reduced again to ferrous salt by the iodide.

It may also be of interest to note here that S. Kikuchi<sup>58</sup> has estimated titanium, after reduction with liquid amalgam (p. 146), by titrating with a standard iodine solution, using 2.N sodium tartrate as buffer. Iron and uranium are said to be non-reactive under the circumstances.

## (6) DIFFERENTIAL VOLUMETRIC METHODS.

### (a) Titanium and Iron.

Apart from the actual separation of titanium and iron, which has been fully considered in Chapter VI(4)(a), several volumetric methods are known, which provide for the direct estimation of either of these two elements in such a way that the presence of the other does not interfere. Although titanium may be titrated in the presence of iron with either a ferric salt or with methylene blue (pp. 145 and 147), a direct estimation of the iron would seem on the whole to be preferable, owing chiefly to the far greater sensitiveness of the titanous salts toward atmospheric oxygen as compared with the corresponding ferrous salts. Moreover, the reductor, when used in the manner prescribed by Lundell and Knowles (p. 143 *et seq.*), can be relied on to give a titer corresponding very accurately to the sum of the titanium and iron; consequently it would seem to be a reasonably safe procedure to obtain the titanium value by difference.

Confining our attention then to the direct estimation of iron in titaniferous substances, wherein a standard solution of potassium permanganate or potassium dichromate is to be used for the titration, two courses are open to the analyst: first, a reducing agent may be selected that does not affect titanium, e.g., hydrogen sulfide, sulfur dioxide, stannous chloride (in hydrochloric acid solution, followed by mercuric chloride),<sup>59</sup> finely divided silver (in sulfuric acid solution containing also ammonium thiocyanate)<sup>60</sup> or mercury (in hydrochloric acid solution),<sup>61</sup> or second, a more energetic reducing agent may be employed and the titanous salt destroyed by the addition of some oxidizing agent too mild to affect the ferrous iron, e.g., zinc (in sulfuric acid solution, followed by bismuth trioxide),<sup>62</sup> titanous sulfate (in sulfuric acid solution, followed by bismuth trioxide)<sup>63</sup> or titanous chloride (in hydrochloric acid solution, followed by copper sulfate).<sup>64</sup> Accordingly, these two cases will be taken up in turn.

#### (\*) Reduction of the Iron, Avoiding the Presence of Titanous Salt.

Hydrogen sulfide gives very good results in the volumetric determination of iron, provided the conditions laid down by Lundell and

Knowles<sup>65</sup> be carefully complied with. Sulfur dioxide is not so satisfactory for highly titaniferous materials; since complete reduction takes place only in a nearly neutral solution, and under these circumstances some titanous acid comes down, which seems to occlude a little ferric iron in an insoluble form. The Zimmermann-Reinhardt method<sup>66</sup> is frequently not applicable to titanium minerals; since many of these are refractory and must therefore be fused in platinum with an appropriate flux. If the solution contain a small quantity of platinum salt, it is practically impossible to tell when the stannous chloride has been added in excess; for, when most of the iron has been reduced, the platinum begins to undergo reduction also, so that instead of becoming colorless with further additions of the reducing agent, as would naturally be expected, the solution takes on a reddish tint owing to the formation of the platinous salt.<sup>67</sup> G. Edgar and A. R. Kemp<sup>68</sup> state that under their conditions silver does not reduce titanium at all, and L. W. McCay and W. T. Anderson, Jr.<sup>69</sup> furnish experiments that prove the indifference of titanium toward mercury at ordinary temperatures.

*The Hydrogen Sulfide Process.* The solution should have a volume of 100 cc. and contain 2.5 per cent of concentrated sulfuric acid by volume. Should the volume exceed this amount, as will often be the case, it is concentrated by evaporation after the addition of a sufficient quantity of sulfuric acid to prevent the precipitation of titanium by hydrolysis.<sup>70</sup> When the bulk has been reduced to something less than 100 cc., the acidity is adjusted to the above given value of 2.5 per cent by volume by partial neutralization with ammonium hydroxide and the volume is made up with water to exactly 100 cc. The solution is now treated with hydrogen sulfide in a covered beaker for 30 minutes at the room temperature and then for 15 minutes longer as it is heated to boiling. The solution is cooled somewhat, and filtered through paper of good quality, which has been previously subjected to thorough washing with hot water,<sup>71</sup> into a flask of convenient size so as to remove any metals of the hydrogen sulfide group (especially platinum). The paper is washed with cold water, and the filtrate is gassed again for 10 minutes with hydrogen sulfide to overcome any reoxidation that the solution may have suffered during filtration. It is preferable that the flask be closed by a ground in tubulated stopper (such as are used with all-glass wash-bottles); for in this way any possible contamination with organic matter from a rubber or cork stopper is avoided. An additional 15 cc. of sulfuric acid (1:1) is then introduced, and the solution is boiled for 30 to 60 minutes, while a stream of carbon dioxide is being bubbled through it,<sup>72</sup> until the volume has been reduced to approximately 50 cc. After cooling in the atmosphere of carbon

dioxide, the solution is diluted to 200 cc. with cold water and titrated at once with standard potassium permanganate.

(\*\*) **Reduction of the Iron Regardless of the Presence of Titanous Salt and Subsequent Oxidation of the Latter.**

Gooch and Newton<sup>73</sup> have shown that a sulfuric acid solution of iron and titanium may be reduced by zinc, the titanous sulfate converted back to titanic sulfate by the addition of copper sulfate, copper oxide or bismuth oxide, the metallic copper or bismuth formed along with any excess oxide removed by filtration and the ferrous sulfate titrated with potassium permanganate. Of these three oxidizing agents, which do not affect ferrous iron, oxide of bismuth seems to be the best.

*The Zinc and Bismuth Trioxide Process.* The solution to be tested should have a small volume (preferably less than 100 cc.) and must be free from hydrochloric acid. There should be present, however, from 10 to 15 cc. of sulfuric acid (sp. gr., 1.84). The reduction is made in a small flask, partially closed with a little funnel or cut off calcium chloride tube,<sup>74</sup> by adding 5 to 10 grams of 30-mesh zinc (roughly weighed) and warming gently from time to time so as to maintain a brisk action until all of the zinc has dissolved; whereupon the solution is promptly cooled by immersing the flask in running water. If the liquid shows a violet color after the disappearance of the zinc, it is perfectly certain that the reduction of the iron to the ferrous condition is complete. With the temperature of the solution at 15-20°C., about 2.5 grams of bismuth trioxide is added and mixed in by swirling the liquid, after which the solution is filtered through paper (previously washed with boiling-hot water—cf. p. 151) and the residue is thoroughly washed with cold water. The filtrate is then titrated with potassium permanganate in the usual manner.

In order to correct for the small amount of iron (and perhaps other reducing substances) that commercial specimens of zinc almost invariably contain, a blank analysis must be made, using the same quantities of reagents and performing all of the operations given above. The permanganate titer, when thus corrected, corresponds to the true amount of iron in the sample.

Instead of using granular zinc in a flask it is also permissible and indeed very convenient to employ the Jones reductor.<sup>75</sup> In this case the instructions given on p. 143 *et seq.* may be followed except that an empty receiver should of course be used.

Newton<sup>76</sup> has investigated further along this line and has demonstrated that ferric sulfate can be immediately and quantitatively reduced by adding a measured volume of a titanous sulfate solution—enough to impart the characteristic violet color of titanous salts to the

entire liquid, thus proving the presence of an excess of the reducing agent. The oxide of bismuth is then introduced, and the remaining operations are carried out as described above. The titanous sulfate should be tested for iron by means of a blank experiment made on a known volume of the solution, and, if present, the proper deduction applied.

The test analyses of Gooch and Newton as well as those of Newton are sufficient to show that both processes are highly accurate.

In like manner, L. Brandt<sup>77</sup> reduces the ferric salt with titanium trichloride and destroys the excess with copper sulfate. He claims that platinum chloride, potassium dichromate and arsenic acid do not interfere, but that arsenious acid must be absent.

### (b) Titanium, Iron and Chromium.

Van Brunt<sup>78</sup> states that titanium, iron and chromium may all be determined volumetrically in the same material in accordance with the following scheme:

The sulfate solution is divided into three aliquot parts. The first portion is passed through the reductor,<sup>79</sup> the deoxidized solution treated with oxide of bismuth, filtered and the filtrate titrated with potassium permanganate. This titer corresponds to the iron only.<sup>80</sup> If preferred, hydrogen sulfide or sulfur dioxide may be used. The second portion is then put through the reductor, the receiver being charged with ferric sulfate solution. This titer is therefore equivalent to the titanium, iron and chromium. The third portion is oxidized with ammonium persulfate, treated with ferrous sulfate solution in excess and titrated back with permanganate, thus obtaining a titer equivalent to the chromium. It is now obvious that, if the sum of the permanganate equivalents of the iron and chromium be subtracted from that of the three constituents combined, the difference will equal the titanium.

## Chapter IX.

### The Analysis of Titaniferous Materials.

#### (1) DETERMINATION OF SPECIFIC GRAVITY.

A knowledge of the specific gravity of minerals and rocks is frequently desired by geologists and mineralogists. In like manner, the technologist who has to do with titanium products that are made artificially may sometimes have need of this quantity, as, for instance, in calculating the bulking figure of titanium pigments (see p. 68). Since, however, the technique is the same for titanium-bearing substances as for other bodies having similar physical properties, no very extensive discussion of methods need be given in a specialized work of this kind.<sup>1</sup>

#### (a) The Suspension Method.

If large pieces of material free from cracks are available, the method of weighing the lumps suspended in water can be employed with advantage.

One or several fragments weighing up to 20 grams may be used for the experiment. The material is held by a fine platinum wire ready for suspension from the balance hook and is placed in a small beaker of distilled water. This, along with a similar beaker containing an equal amount of water, is set in a vessel capable of being evacuated.<sup>2</sup> The receptacle is then exhausted and allowed to remain so over night. In the morning both beakers are placed in the balance case, a thermometer being inserted in the one containing water only, and the substance is weighed immersed in water in the usual manner (see Figure 21, left), and at the same time the temperature is observed. The mass is then taken out of the water and placed in a tared vessel. The wire is removed and weighed again with the same length below the water level as formerly. The sample is now dried, first on the water-bath and then in the oven at 110°C., cooled in a desiccator and weighed. The heating is repeated until a constant weight is obtained. The specific gravity may be calculated by substituting in the formula:

$$S = \frac{W_1}{W_1 - W_2}$$

in which  $S$  = specific gravity,  $W_1$  = weight in air and  $W_2$  = weight in water. To find the specific gravity of the substance as compared with water at  $4^\circ\text{C}$ ., the result must be multiplied by the density of water at the temperature of the experiment.<sup>3</sup> It is not always possible, however, to calculate what the specific gravity would have been, had the solid material been at some other temperature (e.g.,  $20^\circ\text{C}$ .) ; since its coeffi-

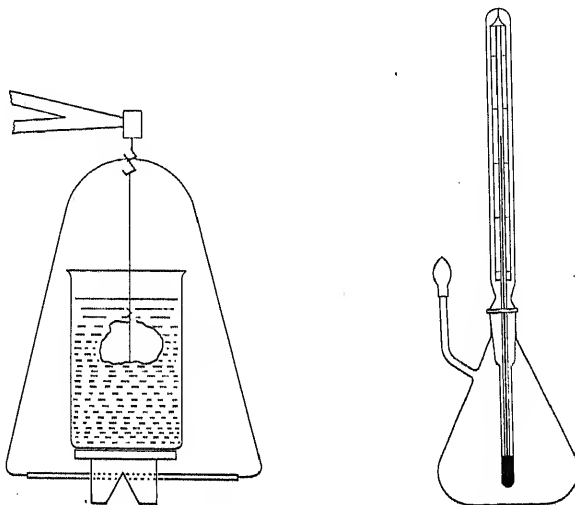


FIG. 21.—Specific gravity apparatus: suspension method (left) and pycnometer (right).

cient of cubical expansion is frequently unknown. Strictly speaking, both the weight of the object and the water displaced by it should be corrected to vacuum before making the above ratio ; but under ordinary conditions this would be an unnecessary refinement. The accuracy of the process is of course enhanced by taking the largest sample that can be conveniently handled.

### (b) The Pycnometer Method.

The pycnometer has the advantage that it can be used with materials in the form of small fragments, being applicable with certain modifications even to powders.<sup>4</sup> The instrument shown in Figure 21 (right) is convenient in that the ground in thermometer will give the temperature of the water (or other liquid) at the time the weighing is made.

The weight of the empty and dry pycnometer is first taken. A considerable quantity (preferably 10-15 grams) of the sample, the particles



of which should not be small enough to cause trouble by floating, is then introduced into the flask and the instrument is again weighed. Distilled water is added until the solid has been completely submerged, and the open pycnometer along with another vessel containing enough water to fill the flask twice is placed in an air-tight chamber and the air pumped out as described in (a). The pycnometer is then filled with the air-free water, wiped dry with a clean linen cloth and weighed as promptly as possible, the temperature being also noted. After emptying the flask of all solid material, the instrument is filled with the same water and weighed again. The specific gravity may now be calculated in accordance with the following formula:

$$S = \frac{W_1}{(W_1 + W_2) - W_3},$$

in which  $S$  = specific gravity,  $W_1$  = weight of solid substance in air,  $W_2$  = weight of pycnometer full of water and  $W_3$  = weight of pycnometer full of solid and water. The chief source of error in the pycnometer method is the gradual loss of weight due to evaporation around the stopper (and cap). If accuracy is desired, therefore, it is necessary that these joints be ground with extreme care. It is also desirable to apply a very thin film of vaseline before making the final weighing.<sup>5</sup>

The specific gravity of titanium pigments should be determined according to "Standard Method of Test for Specific Gravity of Pigments" (D 153-24) of the American Society for Testing Materials.<sup>6</sup>

## (2) PREPARATION OF THE SAMPLE.

In preparing the sample for analysis two cases naturally arise. If the analysis is being made purely for scientific interest, then the object may be to isolate as far as possible a chemically definite substance. This state of affairs prevails in mineralogical studies—in other words, a distinct mineral species is to be investigated. If, on the other hand, the material is to be regarded as an ore, or a technical product whose average commercial value is to be determined, then the sample should be taken in such a way as to be representative of the whole.

### (a) The Isolation of a Definite Mineral.

When the mineral aggregate is of fairly coarse texture, as would be the case in pegmatitic or vein material, it is a comparatively easy matter to break the larger masses down with hammer and anvil so that fragments of the desired mineral can be obtained by hand sorting practically free from admixture. Material selected in this way, however, on further examination by suitable methods is often found to be far from

homogeneous, owing to inclusions, intergrowths, isomorphous replacements, etc. But these are considerations for the mineralogist and petrographer to deal with. The chemist is not usually called on to assume responsibility beyond that of making the analysis on pieces that appear to be reasonably clean as far as the unaided eye can tell.

With fine grained rocks, however, the problem of isolating a single mineral becomes mechanically much more difficult, and the best mode of attack to be employed in any given case depends upon the specific properties of the individual minerals involved.

Having reduced the mass to particles of appropriate size (between No. 10 and No. 16 bolting cloth), certain components may be separated from others by treatment with heavy solutions in the Smeeth apparatus.<sup>7</sup> Thoulet's solution, for instance, which consists of a saturated solution of potassium mercuric iodide in water, has a maximum specific gravity of 3.196, which of course may be lowered by the addition of water to any desired value. In this medium the lighter minerals (such as quartz, feldspar and mica) float, many of the heavier ones (e.g., chrysolite, zircon, titanite, magnetite, hematite, ilmenite, rutile and monazite) sink while pyroxene and amphibole either float or sink according to the variety. Several other heavy solutions are known that may be used in this way. By the proper dilution of these a solution of almost any predetermined density may be obtained up to the very heavy silver thallium nitrate of Penfield, which is liquid at 75°C. and has a maximum specific gravity of over 4.5 which may be reduced by the addition of hot water.<sup>8</sup> It is also possible to prepare heavy liquids by melting certain solid substances.<sup>9</sup>

Another method of separation of somewhat more limited applicability depends upon differences in magnetic susceptibility on the part of the various minerals. Thus magnetite is readily attracted by an ordinary permanent magnet, and several iron-bearing minerals (such as amphibole, pyroxene, chrysolite, epidote, garnet, etc.) can be lifted by the electromagnet. Since the strength of the electromagnet may be varied at will, the ferruginous minerals may to some extent be parted one from another.<sup>10</sup> Rutile is freed from ilmenite by means of the magnetic separator (p. 31), and ilmenite is at least partially separated from magnetite in a similar manner (p. 37).

It is sometimes feasible to break the rock down to the condition of coarse sand, spread a small quantity at a time on a white surface and by means of a magnifying glass and sharp pointed instrument discard all grains that do not appear to consist of the mineral in question. This method, however, is a very tedious one, and is therefore not employed except when others fail.

Other expedients are the operation of panning (as for gold) and

the differential solvent action of certain chemical reagents—a special application of the latter being the removal of apatite from either rutile or ilmenite in nelsonite (p. 34) by treatment with dilute mineral acid.

### (b) The Procurement of an Average Sample.

It is frequently of the utmost importance for commercial reasons and sometimes for scientific reasons as well that every effort be made to procure a sample for analysis that will be truly representative of the original material as a whole. The problem is often fraught with considerable difficulty, and even when the work has been conscientiously done the result may be of somewhat uncertain nature. The subject is more or less adequately treated in various works on analysis.<sup>11</sup> No attempt will be made to give an exhaustive discussion here.

A sufficient amount of the material is first comminuted by whatever means may be necessary to a degree of fineness proportionate to its homogeneity, the size of the particles being made as nearly uniform as possible. It is then thoroughly mixed, divided into four approximately equal parts and the two opposite portions are reserved—the other two being rejected.<sup>12</sup> This fraction of the original quantity of material is crushed still finer, mixed and quartered again. These operations are repeated until a sample small enough for the laboratory has been obtained, which of course will vary greatly according to circumstances; but, roughly speaking, 50 to 100 grams may be regarded as the customary amount. This is comminuted further, if necessary, until the whole of it has been made to pass through a sieve of the proper mesh—it being imperative that the maximum size particle shall be readily acted on by the reagents to be subsequently applied. The sample must now be given a very thorough mixing, after which it is bottled and preserved for the analysis.

### (c) The Comminution of the Material.

Where large quantities of materials are to be comminuted the use of power driven devices is essential, unless an inordinate amount of time is to be spent in performing this kind of labor.<sup>13</sup> In lieu of these conveniences small samples may be prepared entirely by hand.

#### (\*) Minerals and Rocks.

The author has employed for some years a method for reducing minerals and rocks to fine powder which is very much like that of H. S. Washington.<sup>14</sup> It is not particularly laborious, provided the amount of powder to be prepared does not exceed 30 grams.

With the aid of a hammer and anvil (both of hardened steel) the

mass is broken into pieces small enough to enter the chilled steel mortar shown in Figure 22 (left).<sup>15</sup> These fragments are crushed to powder in the mortar by successive poundings with the pestle with as little grinding motion as possible. The powder is then transferred to a 250 cc. glass beaker (without lip), a piece of No. 10 silk bolting cloth (108 meshes to the linear inch)<sup>16</sup> is stretched across the mouth of the beaker and held in place by a rubber band and the whole is inverted and shaken over a large sheet of clean paper. The part that does not

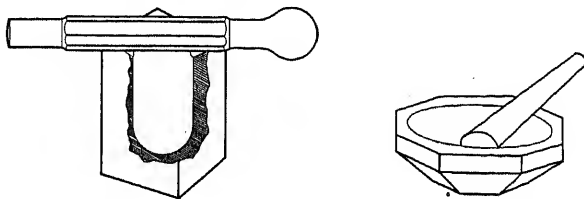


FIG. 22.—Steel mortar (left) and agate mortar (right).

pass through the cloth is returned to the mortar and the operations of crushing and sifting are repeated until only a gram or so of over-size material remains, which is then ground to powder in the agate mortar (Figure 22, right). Needless to say, the size of the particles in this final portion must be at least as small as those that have been put through the sieve. The entire bulk of sample is now poured out on the sheet of paper and mixed by repeatedly trundling it back and forth and from side to side; whereupon it is ready for analysis.

The traces of iron and silica that are inevitably introduced into the sample from the implements used in its preparation are of trifling magnitude, when operating as described above, and may therefore be neglected. The same is true of organic matter derived from the bolting cloth.

#### (\*\*) Metals.

The titanium alloys (such as ferro-titanium, cupro-titanium, manganese-titanium, etc.) are sufficiently brittle to permit being crushed to powder (100 mesh) in a hardened steel mortar. This is also true of other ferro-alloys besides ferro-titanium, hard grades of pig iron, chilled iron, quenched steel, etc. The ordinary varieties of cast iron and steel, however, are highly malleable and must therefore be comminuted by some such process as drilling, milling, shaving, turning, etc.<sup>17</sup>

## (3) ANALYSIS OF NATURAL MATERIALS.

## (a) Oxides and Titanates.

## (\*) The Composition of Rutile and Ilmenite.

The chemical composition of rutile and ilmenite, the two most important titanium minerals, has already been discussed in a brief and general way (pp 26 and 28). The analyses listed in Table VIII are unusually complete—especially I and II; since these specimens were examined spectrographically<sup>18</sup> as well as being subjected to chemical analysis by the ordinary methods.

TABLE VIII.  
ANALYSES OF RUTILE AND ILMENITE.

	I <sup>a</sup>	II <sup>a</sup>	III
SiO <sub>2</sub> .....	0.06	0.14	0.76
Al <sub>2</sub> O <sub>3</sub> .....	Trace <sup>b</sup>	Trace <sup>b</sup>	2.84
Fe <sub>2</sub> O <sub>3</sub> .....	....	10.17	9.13
FeO .....	18.81	34.15	27.81
MgO .....	Trace <sup>c</sup>	4.04	8.68
CaO .....	Trace <sup>b</sup>	Trace <sup>b</sup>	0.23
Na <sub>2</sub> O + K <sub>2</sub> O .....	....	....	0.19
H <sub>2</sub> O, ignition .....	....	....	0.20
H <sub>2</sub> O (110° C.) .....	0.04	0.02	....
TiO <sub>2</sub> .....	80.85	49.34	49.32
P <sub>2</sub> O <sub>5</sub> .....	....	....	Trace
Cb <sub>2</sub> O <sub>5</sub> .....	None <sup>d</sup>	None <sup>d</sup>	....
Ta <sub>2</sub> O <sub>5</sub> .....	None <sup>d</sup>	None <sup>d</sup>	....
Cr <sub>2</sub> O <sub>3</sub> .....	0.03	0.03	0.74
V <sub>2</sub> O <sub>5</sub> .....	0.17	0.03	....
MnO .....	0.14	1.79	0.20
NiO .....	....	Present <sup>e</sup>	....
SnO <sub>2</sub> .....	Trace <sup>b</sup>	Trace <sup>b</sup>	....
	100.10	99.71	100.10

<sup>a</sup> Published by permission of the Director, Virginia Geological Survey.

<sup>b</sup> Detected spectrographically—probably about 0.001 per cent.

<sup>c</sup> Detected spectrographically—amount not estimated.

<sup>d</sup> No trace could be found by spectrographic analysis.

<sup>e</sup> Detected spectrographically—probably about 0.1 per cent.

I. Rutile (with ilmenite intergrowths) from Franklin County, Virginia. Described by Thomas L. Watson in *Am. Mineral.*, 7, 185 (1922). Chemical analysis by Dorothy Getz and spectrographic examination by William F. Meggers.

II. Ilmenite from Franklin County, Virginia (?). Not hitherto published. Chemical analysis by William M. Thornton, Jr., and spectrographic examination by William F. Meggers.

III. Ilmenite from Elliot County, Kentucky. Described by J. S. Diller in *Am. J. Sci.*, (3) 32, 125 (1886). Analysis by T. M. Chatard.

### (\*\*) Preliminary Qualitative Analysis.

In the examination of these, as well as other titanium minerals, a systematic qualitative analysis will seldom be found necessary.<sup>19</sup> A certain amount of preliminary testing, however, taking advantage of both physical and chemical properties, is often desirable so as to ascertain the general nature of the material (cf. pp. 28, 29 and 30), and the identity of any known mineral species may be established by the methods of "determinative mineralogy"—especially those of G. J. Brush and S. L. Penfield.<sup>20</sup> From a study of published analyses, such as those in Table VIII, the analyst will be in a fair position to decide just what constituents to look for in the material submitted to him for examination—certainly as far as definite minerals are concerned. It must be borne in mind, however, that ilmenite from sand deposits (cf. pp. 31 and 34) is apt to contain a little zirconium and possibly rare earths; since its separation from associated minerals (especially zircon) may not be quite complete. Furthermore, in the case of those ingredients that are likely to be present in amounts too small to be determined quantitatively, it is practically necessary to employ a quantitative technique in order to positively answer the question as to whether a certain substance is present or absent: in other words, qualitative analysis, as ordinarily carried out, would be of little avail. Spectrographic evidence, when it can be had, is very valuable in deciding about the minor constituents, and often serves to give some idea as to the probable amounts, thus answering the question (frequently so difficult) as to whether or not a quantitative search for a certain component would be justified. Spectrographic analysis, however, does not become strictly quantitative except through comparison with experimentally established standards.<sup>21</sup>

### (\*\*\*) The Analysis of Rutile (Author's Procedure).

*Determination of Water, Silicon Dioxide, Titanic Oxide and Ferrous Oxide.* A small quantity of the sample (about 1 gram), prepared as described in (2) (c) (\*), is ground in the agate mortar to an excessively fine powder. Five-tenths gram of this is introduced into a 25 cc. platinum crucible, and the water is determined by drying for 1 hour (or to constant weight) at 110°C. and noting the loss in weight.

About 7 grams of potassium pyrosulfate (free from bisulfate)<sup>22</sup> is added to the crucible and the latter heated with its lid on over a small colorless flame so that the flux is just melted and fumes of sulfur trioxide do not appear except when the lid is raised. The contents of the crucible should be occasionally mixed by gently rotating it with the aid of a pair of Blair's<sup>23</sup> tongs. As the fusion continues, the melting point of the flux gradually increases; hence the temperature must be slightly

raised from time to time; but on no account should the charge be heated hot enough to boil. As soon as the molten mass has become perfectly clear and solid particles are no longer visible, the crucible is removed from the source of heat, and by means of a rotary motion the melt is made to solidify in a fairly uniform layer on the sides and bottom of the containing vessel; after which the cooling is finished quickly by placing the crucible on a clean steel slab. By the application of very gentle pressure the cake can usually be made to detach itself from the crucible; whereupon it is transferred as far as possible while dry to a 250 cc. platinum dish. The melt is dissolved in 35 cc. of sulfuric acid (1:1) and a sufficient quantity of water, using a part of the acid to clean the crucible. The solution is then evaporated down on the hot plate until the sulfuric acid fumes freely, taking great care (especially in the latter stages) to avoid loss by spattering. The syrupy liquid is cooled, diluted with 50 cc. of water and the dish is warmed to coagulate the silicic acid. Only in this way can the silicon dioxide be completely recovered. Simple solution of the pyrosulfate melt in dilute acid is not sufficient, as the experiments of W. F. Hillebrand<sup>24</sup> have shown. The solution is filtered through a small quantitative paper, the last trace of silicic acid is removed from the dish by wiping the inner surface with small pieces of ashless filter paper and the residue is washed very thoroughly (about fifteen times with cold water and ten times with hot) so as to get rid of all alkali salt. The filter with its contents is placed in the platinum crucible and the ignition is carried out in the usual manner, finally applying the full flame of a Méker burner for 20 minutes. After taking the weight, the silicon dioxide is volatilized as described on p. 124 and the crucible (containing the non-siliceous residue) is heated for another 20 minutes over the same Méker burner—the loss in weight being equivalent to the amount of silicon dioxide originally present. The small amount of titanium and iron oxides is gotten into solution by fusing with a little potassium pyrosulfate (about 2 grams will usually suffice) and taking up the melt in 5 cc. of sulfuric acid (1:1) and enough water to effect solution, and this is added to the filtrate obtained above. The entire solution, being at the temperature of the working room, is transferred to a carefully calibrated flask of 250 cc. capacity, the remaining volume made up by adding water from a burette and two 100 cc. portions are transferred to beakers by means of a pipette, the delivering capacity of which is accurately known.<sup>25</sup> The solution left in the flask along with the pipette rinsings constitute another aliquot part (1/5) of the sample and should therefore be reserved for another determination.

*Optional Procedure No. 1* (Gravimetric Determination of the Iron). Two grams of citric acid is added to a 100 cc. aliquot part,

the solution is made neutral to litmus paper by the addition of freshly prepared ammonium hydroxide (i.e., free from silicic acid) and then made acid again with 2.5 cc. of sulfuric acid (1:1). While still somewhat warm, the solution is gassed with hydrogen sulfide till practically saturated at the room temperature. The small precipitate of platinum sulfide (with some free sulfur) is removed by filtration through a paper of close texture and the residue is subjected to the ordinary course of washing with cold water. The iron in the filtrate is then precipitated as ferrous sulfide and finally weighed as ferric oxide according to p. 96.<sup>26</sup>

In the filtrate from the ferrous sulfide the titanium is determined by the cupferron process as described on pp. 90, 96 and 98.

*Optional Procedure No. 2* (Volumetric Determination of the Iron). If one wishes to determine the iron volumetrically in a separate aliquot part, and this doubtless is the better alternative (cf. p. 98), it is hardly necessary to filter off the sulfide of platinum; since J. Riban<sup>27</sup> has shown that freshly precipitated platinic sulfide is nearly insoluble in ammonium sulfide, but that it dissolves in large quantity when mixed with other sulfides of either the tin or copper groups. Otherwise the procedure for titanium is the same.

In the other 100 cc. aliquot part, it being well to use the 50 cc. portion for verifying the titanium value, the iron may be determined by any of the methods given in Chapter VIII (6) (a).<sup>28</sup> The method of F. A. Gooch and H. D. Newton (p. 152) is highly satisfactory; or, if a solution of titanous sulfate be at hand, Newton's process (p. 152) may be used with economy of time. It is also an easy matter to determine the iron directly by titration with a standardized solution of titanous chloride or sulfate.<sup>29</sup>

Rutile being insoluble in acids, there is no method known for deciding how much of the iron was originally present in the bivalent and trivalent conditions respectively. It is customary, therefore, to determine the total amount of iron and report it as ferrous oxide.

*Determination of Manganous Oxide.* From 0.5 to 1 gram of the finely powdered sample is fused with potassium pyrosulfate until the decomposition seems to be complete. The melt is treated with 10 cc. of sulfuric acid (1:1) and 50 cc. of nitric acid (1:3), warming to effect solution. The small residue of unattacked mineral is collected on a small filter paper and washed thoroughly with hot water, the filtrate and washings being received in a basin of Pyrex glass. The residue is ignited in a platinum crucible, treated with hydrofluoric and sulfuric acids so as to volatilize the silicon dioxide (p. 124) and fused with a small lump of the pyrosulfate. Meanwhile, the first solution, representing nearly all of the assay, is evaporated on the steam-bath until all



of the nitric acid has been expelled. The second melt is dissolved in nitric acid (1:3), the solution transferred to the evaporating basin and the crucible rinsed with some of the same acid—using just 50 cc. in all. The basin is heated till no further solvent action seems to be taking place, and the entire solution (along with some white insoluble titanic acid) is transferred to a 300 cc. Erlenmeyer flask, using a small additional quantity of nitric acid (1:3) to rinse the basin. The manganese is then determined by the sodium bismuthate method.<sup>30</sup> Five-tenths gram of sodium bismuthate is introduced into the flask and the solution is boiled for 5 minutes. Ferrous ammonium sulfate (or other reducing agent) is then added gradually until the liquid has become perfectly clear. The solution is boiled for 2 minutes to expel oxides of nitrogen, after which it is cooled to room temperature (20°C.). An excess of the bismuthate (0.5 to 1 gram) is added and the materials are thoroughly mixed by shaking the flask for half a minute. Fifty cc. of nitric acid (3 per cent by volume) is introduced in such a way as to wash down the sides of the flask, and the surplus bismuthate is removed by filtration through asbestos,<sup>31</sup> the residue being washed with the 3 per cent nitric acid until the sum total of filtrate and washings equals 200 cc. Twenty-five cc. of ferrous ammonium sulfate (0.03 to 0.05 N) is then added by means of a transfer pipette and the excess is immediately titrated with potassium permanganate of approximately the same normality, which has in turn been standardized against sodium oxalate (p. 141). A blank experiment must be carried out in order to ascertain the reducing power of the ferrous ammonium sulfate solution. This is done by adding a little bismuthate to 50 cc. of nitric acid (1:3), agitating, diluting with 50 cc. of 3 per cent nitric acid, filtering, washing and titrating in accordance with the above technique. This procedure serves incidentally to test the efficiency of the filter and should therefore be performed prior to the main experiment.

The filtering device shown in Figure 23 can be used with advantage in the bismuthate process; since, in the event of a turbid filtrate, the liquid may be returned to the reaction vessel by an obvious manipulation of the stop-cocks without breaking any connections—any sediment at the apex of the tap funnel being washed out by several portions of filtrate after it has become clear.

*Determination of Chromic Oxide and Vanadium Trioxide.* The chromium and vanadium are determined on the same portion of material by the method of Hillebrand.<sup>32</sup> Five grams of the mineral powder is thoroughly fused with 20 grams of sodium carbonate and 3 grams of sodium nitrate in a large platinum crucible (60 cc. capacity)—increasing the heat gradually during the early stages, so as to avoid excessive effervescence, but finally bringing the charge to the highest

temperature attainable with a good blast lamp and maintaining it so for some time. The cooled mass is digested with hot water till completely disintegrated, and, after adding a few drops of alcohol to precipitate manganese, the aqueous extract is separated from the insoluble matter by filtration. The filtrate is made nearly neutral with nitric acid (1:3)—the amount to be added being gaged by titrating exactly 20 grams of the same sodium carbonate that was used in the fluxing mixture—and evaporated to approximate dryness on the steam-bath. It is important to avoid overstepping neutrality at this point because of the

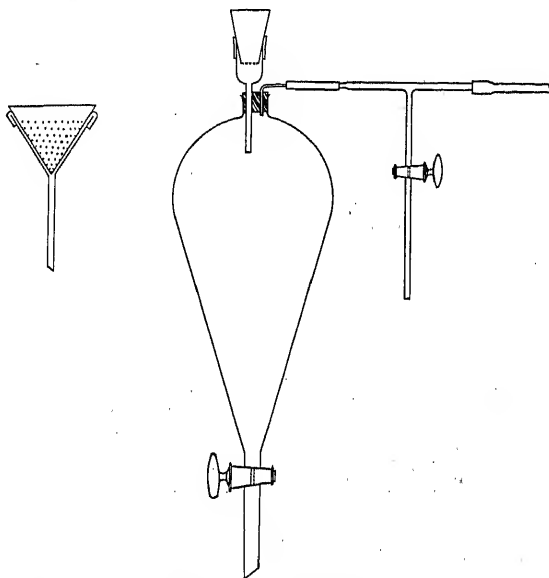


FIG. 23.—Filtering tube.

reducing action of nitrous acid. The salts are taken up in a sufficient quantity of hot water, and any solid material that may have separated during the evaporation is collected on a small filter and worked over to recover traces of chromium and vanadium that may have been retained by it. This residue is therefore ignited in a platinum crucible, treated with hydrofluoric and sulfuric acids to remove silicon dioxide (p. 124), fused with about 2 grams of sodium carbonate, the melt dissolved in water, the extract nearly but not quite neutralized with nitric acid and after boiling the solution added to the main one. An almost neutral solution of mercurous nitrate is now added to the cold alkaline solution until no further precipitation occurs. In case an unduly large precipitate should form, the alkalinity may be reduced by the careful addition

of nitric acid until the solution ceases to become turbid on the further addition of a drop of mercurous nitrate. The precipitate is coagulated by heating the solution, collected on paper and washed with a 2 per cent solution of ammonium nitrate. The filter and contents are dried, the paper burned by itself (as free from precipitate as possible), the ash added to the main portion of precipitate contained in a platinum crucible and the whole ignited under the hood till the mercury has been completely vaporized.<sup>33</sup> The residue is fused with 2 grams of sodium carbonate, the melt leached with water, the solution passed through a filter and the filtrate and washings made up to a volume of 50 cc. in a volumetric flask. The chromium is then determined colorimetrically by comparison with a standard solution in the Schreiner colorimeter (p. 130, Figure 17).

The standard chromium solution is prepared by dissolving 0.25525 gram of potassium chromate (previously recrystallized and dried at 130°C.) in water, adding a little sodium carbonate and making the volume up to exactly 1000 cc.

The entire test solution is transferred to a beaker, sulfuric acid is added until an acidity of 2.5 per cent of concentrated acid by volume has been reached and hydrogen sulfide is passed in, while warming the solution, so as to precipitate any traces of arsenic, molybdenum or platinum<sup>34</sup> that might be present and reduce the vanadium and chromium to the quadrivalent and trivalent conditions respectively. The cool solution is clarified by filtration and caught in a flask of suitable capacity, and the hydrogen sulfide is boiled out, the removal of the last trace being assisted by bubbling carbon dioxide through the liquid.<sup>35</sup> The deoxidized solution is then titrated while hot (70° to 80°C.) with weak potassium permanganate (0.01 to 0.02 N). After obtaining the end-point, the vanadic acid is again reduced to the divanadyl sulfate, but this time by means of sulfur dioxide,<sup>36</sup> the excess of reducing agent expelled by boiling and the solution titrated with permanganate as before. The second titer is apt to be a little lower than the first and is to be taken as correct.<sup>37</sup>

It is scarcely necessary to seek further confirmation of the presence of vanadium; since the author has never failed to find both chromium and vanadium in all specimens of rutile and ilmenite thus far examined.<sup>38</sup> If, however, it is desired to apply a qualitative test, the ammonium bisulfide reaction may be tried in the following manner: The above solution, or a portion thereof, is made distinctly ammoniacal and then gassed with hydrogen sulfide till fully saturated with respect to the latter. The development of a beautiful cherry-red color indicates vanadium. The test is a very delicate one—the author having been able to detect by it as little as 0.000006 gram of vanadium trioxide with cer-

tainty. The hydrogen peroxide test, recommended by Hillebrand<sup>39</sup> for silicate rocks, is much less sensitive—certainly when applied to non-aluminous materials. Moreover, in the ammonium bisulfide reaction vanadium could not possibly be confused with titanium (cf. p. 61).

The value thus obtained for vanadium is subject to error when much chromium is present. Whenever the chromium exceeds 0.005 gram, therefore, a correction should be applied; since a measurable amount of the permanganate is consumed by the chromium. This is done, according to Hillebrand,<sup>40</sup> by adding permanganate to an equal quantity of chromic sulfate under as nearly as possible the same conditions. The small amount of permanganate used in this way is of course subtracted from the main titer obtained above.

Having thus determined the vanadium, the value should be used to correct the percentage of iron (p. 163). The valence of the vanadium will depend upon the method employed in reducing the iron. If the ferric salt is reduced by means of zinc or titanous sulfate and the solution is treated with bismuth trioxide, the vanadium will be in the trivalent condition, provided the solution be cool and contain 10 per cent of concentrated sulfuric acid by volume.<sup>41</sup> Milder reducing agents, e.g., hydrogen sulfide and sulfur dioxide, carry the vanadium down from the quinquevalent to the quadrivalent stage only, and the same is doubtless approximately true in direct titrations with standard solutions of titanous chloride (or titanous sulfate).<sup>42</sup>

*Determination of Stannic Oxide.* There does not seem to be any really satisfactory method known for determining tin in rutile and related minerals. F. L. Hess and R. C. Wells,<sup>43</sup> in their analysis of strüverite, attempted to estimate the tin in four different ways and obtained rather discordant results, the highest value being more than double the lowest. From the work of Hess and Wells it appears likely that the methods of A. Hilger and H. Haas (p. 122) and W. B. Giles<sup>44</sup> give values that are too low. Moreover, the process of C. Marignac<sup>45</sup> is probably not based on sound principles. The two following procedures, which were suggested to the author by F. W. Clarke,<sup>46</sup> are given here, as they seem to reveal promising lines along which the problem may be attacked; but further study is required before any positive statements can be made in regard to the accuracy of either. First: the mineral is fused with sodium pyrosulfate (preferably in a quartz crucible), the melt dissolved in 5 per cent sulfuric acid by volume, enough tartaric acid added to prevent any precipitation when the solution is neutralized and, after adjusting the acidity, the tin thrown out by hydrogen sulfide. Second: the solution, obtained as in the first instance, is treated with sodium hydroxide in considerable excess, the precipitate of iron, titanium, etc., filtered off and the tin precipitated

in the acidified filtrate with hydrogen sulfide. In either case the tin should be purified by reduction in hydrogen, solution in hydrochloric acid and reprecipitation as sulfide. Of all the methods tried on strüverite by Hess and Wells the second of the two preceding seems to have been the most successful.<sup>47</sup>

There should be no special difficulty in obtaining a qualitative test for tin, should it happen to be present, by getting the mineral into solution by fusion with alkali pyrosulfate and treating with hydrogen sulfide. Other members of the hydrogen sulfide group are not likely to occur in minerals of this kind. It is desirable to avoid fusions in platinum as much as possible, as the separation of tin from platinum is perhaps as difficult (if not more so) as from any of the constituents of the mineral. Furthermore, it is important that, in testing for tin with hydrogen sulfide, the acidity of the solution be properly adjusted. Accordingly, 1.5 cc. of sulfuric acid (sp. gr., 1.84) should be present for every 100 cc. of the solution.<sup>48</sup>

(\*\*\*\*) **The Analysis of Ilmenite (Author's Procedure).**

*Determination of Water, Silicon Dioxide, Titanic Oxide and Total Iron Oxides.* These four determinations are carried out exactly as described under the analysis of rutile (p. 161). In so far as ilmenite contains less titanium and more iron than rutile, it is well to make the volumetric iron determination on the 50 cc. aliquot part and the titanium determination on either or both of the 100 cc. portions, the precipitate of ferrous sulfide being of course available for verifying the iron value.

*Determination of Aluminum Oxide, Calcium Oxide and Magnesium Oxide.* One gram of the finely powdered mineral is fused with about 15 grams of potassium pyrosulfate in the manner given above (p. 161). The melt is dissolved with 25 cc. of sulfuric acid (1:1) and a sufficient quantity of water. It is not necessary to render the silicic acid completely insoluble at this point (cf. p. 162); hence the solution is filtered at once, the small residue of unattacked mineral being collected on a filter and thoroughly washed. This residue is ignited in contact with the paper in a platinum crucible, the silicon dioxide removed by volatilization (p. 124) and the non-siliceous residue brought into solution by fusion with a small lump of potassium pyrosulfate and treatment of the cooled melt with 5 cc. of sulfuric acid (1:1) and enough water to effect solution. The two solutions being united, 10 cc. of nitric acid (1:3) is added to insure the oxidation of all the iron,<sup>49</sup> 5 grams of ammonium chloride is introduced and pure ammonium hydroxide is carefully added to the hot solution by means of a burette or dropping funnel until the escaping vapors show a very faint alkaline reaction to sensitive litmus paper.<sup>50</sup> After heating and stirring for a little while

(not more than a minute), the solution is filtered through a 15 cm. paper, the beaker rinsed and the precipitate washed two or three times with a hot 2 per cent solution of ammonium nitrate.<sup>51</sup> It is not necessary to transfer the precipitate completely to the filter nor to subject it to thorough washing at this stage. As much of the precipitate as possible is returned to the original beaker with the aid of a platinum spatula, and the remainder is dissolved by running hot nitric acid (1:3) through the filter—the runnings being made to wash down the sides of the beaker and in part directed against the stirring rod. The filter is thoroughly washed with hot water, the contents of the beaker warmed till complete redissolution of the precipitate has occurred, the spatula rinsed and removed and, after adding a liberal amount of macerated filter paper, the precipitation with ammonium hydroxide is repeated. The precipitate is completely transferred to the same filter paper (if it still be in good condition) and washed twelve or fifteen times with the hot ammonium nitrate solution. The two filtrates are evaporated separately (preferably in platinum basins) to volumes of 100 cc. or slightly less and tested for completeness of precipitation by the addition of a few drops of ammonium hydroxide. In case a small precipitate forms, as will usually happen with the second filtrate, it is collected on a small paper and thoroughly washed with hot ammonium nitrate and added to the main precipitate. If need be, both solutions are passed through the same filter, the second serving as preliminary wash water for the first. These operations should yield, on the one hand, a precipitate containing all of the aluminum, iron, titanium, phosphoric acid, chromium, vanadium and in all probability a small part of the manganese and, on the other hand, a filtrate containing all of the calcium, magnesium, the greater part of the manganese and all of the nickel, should this constituent happen to be present.

The precipitate is ignited in a platinum crucible, finally blasting for 10 minutes, and the weight taken. If now the amount of silicon dioxide in the precipitate be determined as described under rutile (pp. 161-2) and the manganese<sup>52</sup> by the colorimetric method of H. E. Walters<sup>53</sup> (see below, p. 171), the aluminum may be calculated as the difference; since the iron, titanium, phosphoric acid, chromium and vanadium are (or will be) known. The estimation of aluminum by difference, however, leaves much to be desired in the present case, wherein it makes up a comparatively small part of the ammonium hydroxide precipitate. In fact, the error thrown on the aluminum in this way, when only a very small amount of it is present, may be, relative to its actual amount, enormous. On the other hand, those methods aiming at a direct determination of aluminum that are to be found in the literature do not seem to have been thoroughly examined with regard to their applica-

bility to materials of this kind, viz., those containing large amounts of both iron and titanium but very little aluminum. The following methods are given with the idea that they may suggest to the analyst certain definite lines along which the problem may be attacked. According to W. W. Scott<sup>54</sup> in the filtrate from the titanitic acid precipitate obtained by C. Baskerville's process (pp. 91 and 104) the aluminum may be separated from iron by means of sulfurous acid and phenylhydrazine (pp. 93 and 105), any phosphoric acid in the aluminum precipitate being determined and its weight deducted. R. K. Murphy<sup>55</sup> separates aluminum from iron and titanium by the fusion process of L. Weiss and H. Kaiser (p. 108) and then precipitates it by neutralization of the filtrate with acid. J. Brown,<sup>56</sup> in analyzing zircon and baddeleyite, precipitates the iron, zirconium and titanium with cupferron, and, after destroying organic matter in the filtrate by treatment with sulfuric and nitric acids, separates aluminum from manganese by two precipitations with ammonium hydroxide in the presence of ammonium chloride. None of the above procedures, however, make any provision for the possible presence of chromium and vanadium. In addition to these, it does not seem unlikely that some of the methods that have been employed at the Bureau of Standards<sup>57</sup> for determining aluminum in iron ores might prove useful, at least in part, when applied to the analysis of ilmenite and similar materials. Thus, in order to avoid handling so large a cupferron precipitate, the bulk of the iron might be removed by an ether extraction (p. 100) or by electrolyzing the nearly neutral sulfate solution, using a mercury cathode.<sup>58</sup> The titanium could then be precipitated by cupferron and the aluminum determined in the filtrate according to Brown (see above). The weight of the final precipitate should of course be corrected for phosphoric and vanadic acids.

*Optional Procedure No. 1 (Presence of Nickel).* The combined filtrates from the two ammonium hydroxide precipitations are transferred to a flask (preferably the wide-mouth Erlenmeyer style), an amount of ammonium hydroxide equivalent to 2 or 3 cc. of ammonia water (sp. gr., 0.90) is added in excess and the solution is saturated with hydrogen sulfide. A second like quantity of ammonium hydroxide is added, the flask is filled to the neck and stoppered and the precipitate is allowed to settle for a period of not less than 12 hours (better 24, or even longer). The sulfides are then collected on a small paper and washed with water containing both ammonium chloride and ammonium sulfide. The precipitate, which consists of the sulfides of nickel, manganese and platinum, is ignited in a porcelain crucible, the ash is dissolved in a little aqua regia and the solution is evaporated with hydrochloric acid to the complete decomposition of the nitric acid. After sufficient dilution, the platinum is precipitated by gassing the warm

solution with hydrogen sulfide, and the nickel is determined in the filtrate by the dimethylglyoxime method.<sup>69</sup>

*Optional Procedure No. 2* (Absence of Nickel). In the absence of nickel the ammonium sulfide treatment may be omitted and the test for calcium made at once. For this purpose the solution is made distinctly ammoniacal and 10 cc. of ammonium oxalate (saturated solution) is added, the contents of the beaker being kept hot so as to render the precipitate of calcium oxalate filterable. If a precipitate forms on standing (about 12 hours), it is collected on paper, washed slightly, redissolved in dilute nitric acid and the calcium reprecipitated by ammonium hydroxide and a small extra quantity of ammonium oxalate. The second precipitate is washed with a hot 1 per cent solution of ammonium oxalate and ignited in a platinum crucible, finally applying the blast for 5 minutes.

The two filtrates from the calcium oxalate are combined, a large excess of sodium ammonium phosphate (25 cc. of a 10 per cent solution) is added and ammonium hydroxide (sp. gr., 0.92) is stirred in to the extent of about one-tenth of the final volume. The beaker is set aside for 12 to 24 hours; when the liquid is passed through a paper filter without disturbing the precipitate any more than necessary, and the latter is washed a few times with ammoniacal water (made by diluting one volume of ammonia solution of sp. gr., 0.92 with nine volumes of water). The precipitate is then redissolved in 20 to 25 cc. of warm nitric acid (1:5), and the paper is washed with water. A few drops of the phosphate reagent are now added, ammonium hydroxide is introduced dropwise till the solution has been made neutral and, as soon as the crystalline ammonium magnesium phosphate has formed, about 5 cc. of the same ammonia solution is added in excess. After thorough stirring, the beaker is again allowed to stand for 3 to 6 hours; whereupon the precipitate is collected on a fresh paper and washed about ten times with the above-mentioned washing solution. The paper and precipitate are placed in a tared platinum crucible and very thoroughly dried in the oven at 110°C. The paper is very slowly charred over a small flame, the carbon burned away at a higher temperature and the ignition continued for 10 minutes longer with the full power of a good Tirrill burner.

Unless the manganese has been removed as sulfide (p. 170), the weight of the magnesium pyrophosphate must be corrected for whatever quantity of manganese that it may happen to contain on the assumption that the latter is present in the form of manganous pyrophosphate. If the amount of manganese is small, this may be most conveniently done by the color test of Walters.<sup>60</sup>

The precipitate is dissolved in 10 cc. of sulfuric acid (1:1) and



20 cc. of nitric acid (1:1). Ten cc. of silver nitrate (0.3 per cent solution) is added for every 0.001 gram of metallic manganese, followed by an additional 10 cc. of sulfuric acid (1:1), about 2 grams of solid ammonium persulfate is introduced and the solution is heated over a low flame. Soon after the formation of permanganic acid has begun, as indicated by the development of the purple color, the vessel is removed from the source of heat and immersed in cool water. The solution is then made up at room temperature to a definite volume (100 to 250 cc., depending upon the amount of manganese present) in a measuring flask and the color matched against that of a standard manganese solution similarly treated in the Schreiner colorimeter (p. 130). A standard solution of manganous sulfate containing 0.002 gram of manganous oxide in 10 cc. may be prepared by treating the calculated volume of a standard permanganate solution with 20 cc. of sulfuric acid (1:1) and sulfurous acid at a dilution of 260 cc., the reducing agent being added drop by drop until the color just disappears, and making up the volume with water to exactly 500 cc. Ten, 20 or 30 cc. of this solution is treated with the requisite amount of silver nitrate, 10 cc. of sulfuric acid (1:1) is added and, after oxidizing the manganese with 2 grams of ammonium persulfate in the manner given above, the resulting solution is diluted to 100 cc. in a volumetric flask.<sup>61</sup>

In case the manganese in the pyrophosphate is large in amount, it is better to dissolve the precipitate in nitric acid (1:3) and make the determination by the sodium bismuthate method (p. 163).

Recent work by A. W. Epperson<sup>62</sup> has shown that, if ammonium persulfate be added to the test solution just before making the ammonium hydroxide precipitation, practically all of the manganese enters the precipitate and that, after two precipitations, all of the calcium will be in the filtrate. In consideration of these facts, this would seem to be the better procedure to follow in analyzing ilmenite as compared with that given above, especially when the amount of manganese present is at all considerable and the estimation of nickel is not desired; since the determinations of calcium and magnesium would be rendered more accurate.

*Determination of Ferrous Oxide.* The determination of the ferrous iron in difficultly soluble minerals is accomplished either by the sealed tube digestion method of A. Mitscherlich<sup>63</sup> or by solution in a mixture of sulfuric and hydrofluoric acids as originally proposed by J. P. Cooke, Jr.<sup>64</sup> The author's experience with Virginia ilmenites has shown that they are far more readily opened up by boiling with a mixture of hydrofluoric and sulfuric acids than by digestion in a sealed tube with dilute sulfuric acid alone.<sup>65</sup> Moreover, the procedure of Cooke, either in its original form or as modified by more recent investigators,<sup>66</sup>

is inferior in point of convenience to the simpler method of J. H. Pratt.<sup>67</sup> In pursuing the latter technique, the acid mixture is maintained in active ebullition instead of being heated below boiling with the result that the mineral is fully decomposed in a much shorter time, even though the assay be used in coarser powder; for these reasons the Pratt method yields results that are on the whole as accurate as those obtained by the Cooke process, in spite of the fact that less adequate means are employed for protecting the solution against atmospheric oxidation.<sup>68</sup> As R. Mauzelius<sup>69</sup> has pointed out, the ferrous iron in minerals and rocks undergoes oxidation with fine grinding; hence the size of the particles should be no smaller than is necessary to ensure complete attack by the reagents in a reasonable length of time. Thus R. B. Gage<sup>70</sup> states that magnetite grains having a maximum diameter of 0.08 mm. can be decomposed in about 5 minutes, and the author has found that ilmenite powder, prepared as described above (p. 158), seems to suffer complete dissolution in 7 minutes; since finer powder similarly treated gave a lower value for the percentage of ferrous oxide. The following modification of the Pratt method is believed to be satisfactory:

Five-tenths gram of the 108 mesh powder (p. 158) is placed in a 60 cc. platinum crucible,<sup>71</sup> a spiral of platinum wire is introduced to prevent bumping, the charge is moistened with 10 cc. of water and 10 cc. of sulfuric acid (1:1) is then added. By means of a slender glass tube carbon dioxide is fed into the crucible, the lid being raised a little on one side. While the air is being displaced, the contents of the crucible is cautiously heated with a small flame, best by manipulating the lamp with one hand; but before boiling occurs the gas tube is removed and the lid, which should make a snug fit with the crucible, is made to resume its normal position, and the heating is continued until the liquid boils and steam issues visibly around the mouth of the vessel. The flame is temporarily moved aside, and after a moment's cooling the lid is drawn a little to the left with a pair of tongs while 5 to 10 cc. of hydrofluoric acid<sup>72</sup> is poured into the crucible from the right side. The lid is replaced as quickly as possible, the heating is recommenced and gentle ebullition is maintained for 5 to 10 minutes, or even longer, depending upon the refractory nature of the material—7 minutes being usually sufficient in the case of ilmenite. Without changing the position of the flame and without removing the lid, the crucible is grasped with a pair of Blair tongs and promptly plunged into 500 cc. of recently boiled and cooled water containing 10 cc. of sulfuric acid (1:1) and 5 grams of boric acid. The titration is made at once with a standard solution of potassium permanganate. In the presence of boric acid it is quite permissible to work in glassware and the end-point is not evasive, as O. L. Barnebey<sup>73</sup> has shown.

Organic matter, sulfur in the form of sulfides and vanadium may vitiate the result for ferrous iron. The first of these is not likely to occur in ilmenite, the influence of the second has been discussed at some length by Hillebrand <sup>74</sup> and, since the condition of vanadium in most minerals is not positively known, no correction can be intelligently applied. <sup>75</sup>

O. Hackl <sup>76</sup> has demonstrated that, instead of making a determination of the ferrous iron in the manner given above and calculating the ferric iron by difference (the total amount of iron being otherwise known), it is about equally feasible to estimate the ferric iron directly by titration with a standard solution of titanous chloride.

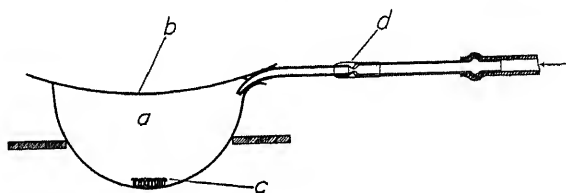


FIG. 24.—Apparatus for the determination of ferrous iron in minerals.

The apparatus shown in Figure 24 has been used by the author for determining ferrous iron in minerals (and in a few cases for ferric iron by Hackl's method) and has been found to give reasonably good protection. It consists of a "palau" <sup>77</sup> dish *a* of 50 cc. capacity with a "watch-glass" cover *b* and a small platinum tube passing through the narrow lip open, the platinum tube being sealed to a glass tube at *d*. The platinum wire spiral *c* is also shown in the illustration. In using the apparatus it is desirable to press the cover down upon the dish as tightly as may be by laying some heavy object on it. With this contrivance it is possible to maintain a steady stream of carbon dioxide throughout the entire process of dissolving the substance in the acid mixture; with this exception the manipulation is about the same as that described above. It may also be remarked that liquids are more apt to boil smoothly in a vessel of this shape than in one of deeper form with flat bottom like the ordinary crucible.

*Determination of Manganous Oxide.* The manganese in ilmenite is determined by the sodium bismuthate method as in the case of rutile (p. 163).

*Determination of Chromic Oxide and Vanadium Trioxide.* The chromium and vanadium are determined by the method of Hillebrand as described under rutile (p. 164). It must be borne in mind, however, that ilmenite, being a less acidic material than rutile, is not so readily fluxed by the carbonate-nitrate mixture. F. J. Pope, <sup>78</sup> in connection

with a study of magnetic iron ores from Eastern Ontario, has given some directions for estimating vanadium in more or less titaniferous magnetites.<sup>79</sup> He fuses 10 grams of the finely pulverized ore with 50 grams of sodium carbonate and 6 grams of sodium nitrate. The ratio of carbonate to nitrate is thus twenty-five to three instead of twenty to three, as prescribed by Hillebrand. The ore and flux are first made into an intimate mixture, and this is charged into the platinum crucible in small portions at a time, each addition being thoroughly melted before the next is introduced. In this way the infusible ferric oxide is scattered throughout the mass instead of being agglomerated in a single large lump, which happens if all is fused at one time. Finally, the entire charge is heated for an hour at the highest temperature that it is possible to attain with two blast-lamps. After leaching the melt with hot water, the residual matter should be subjected to another fusion in order to make sure that the entire amount of vanadium has been extracted. Since in Hillebrand's method the chromium is determined colorimetrically and the vanadium titrimetrically, it would seem permissible to work with only half the sample employed by Pope; consequently the charge would become: 5 grams of the mineral (the more finely powdered the better), 25 grams of sodium carbonate and 3 grams of sodium nitrate.

*Determination of Phosphorus Pentoxide.* The determination of phosphorus in ilmenite may be accomplished by following the procedures given under titaniferous iron ores (see below, p. 178).

*Determination of Sulfur.* Ilmenite may contain sulfur in the form of enclosed sulfide minerals (especially pyrite), which are not always visible to the naked eye. The determination of total sulfur in ilmenite is carried out in the manner given below under titaniferous iron ores (p. 181).

*Determination of Potassium and Sodium Oxides.* As far as the author is aware, ilmenite free from admixed gangue does not contain the alkali metals. However, should their presence be suspected and their estimation desired, the well-known method of J. L. Smith<sup>80</sup> may be used. The alternate procedure of igniting the mineral powder with a mixture of anhydrous barium chloride and barium carbonate, as proposed by G. H. Whiteford,<sup>81</sup> is also satisfactory.

*Determination of Water (above 110°C.)* It is not permissible to determine the total amount of water in ilmenite by the method of loss on ignition, since the sample undergoes an indefinite gain of weight when heated in air owing to the oxidation of the ferrous iron. It is therefore necessary either to employ the simple method of Penfield<sup>82</sup> or to collect the water, after its expulsion at a sufficiently high temperature (bright red heat), in a weighed tube containing calcium chloride

(or other suitable absorbent). In case the latter expedient is adopted, only the water that is lost above 110°C. should be determined, the sample being deprived of its hygroscopic moisture by thorough drying prior to the ignition. By way of apparatus, the combustion tube and furnace may be used, the water vapor being swept forward by a current of dry air (cf. Figure 26). Moreover, the tubulated crucible of Gooch<sup>83</sup> has certain advantages. These more complicated contrivances, however, are scarcely superior either in point of convenience or accuracy to the Penfield tubes, which the operator can readily make for himself from materials of trifling cost.<sup>84</sup>

(\*\*\*\*\*) **Other Methods for the More or Less Complete Analysis of Rutile and Ilmenite.**

P. W. and E. B. Shimer<sup>85</sup> give a method for analyzing rutile, which provides for the estimation of the siliceous residue, total iron and titanium. About 0.1 gram of the sample is gotten into solution by fusion with potassium bisulfate and digestion of the melt in 15 cc. of sulfuric acid (1:1) and a sufficient amount of water (p. 161). The undissolved matter is collected on a filter, washed, ignited and its weight reported as "insoluble residue". The iron is then determined in the filtrate by reduction with hydrogen sulfide and titration with potassium permanganate (p. 151). Finally, the titrated solution is passed through a Jones reductor and the value for titanium obtained oxidimetrically by means of a standard solution of ferric ammonium sulfate, using potassium thiocyanate as indicator (p. 146).

E. W. Hagmaier<sup>86</sup> has published processes for the determination of silicon dioxide, total iron and titanium in rutile. Five-tenths gram of the powdered mineral is opened up by a pyrosulfate fusion and the melt is extracted with 150 cc. of warm 10 per cent sulfuric acid. It is taken for granted that the entire amount of silicic acid is present in the insoluble residue—an assumption which Hillebrand has shown to be erroneous, unless the solution be evaporated to the fuming point of sulfuric acid (p. 162). The true amount of silicon dioxide contained in the washed and ignited residue is determined by treatment with hydrofluoric and sulfuric acids in the usual way (p. 124), and the small residue of non-siliceous matter is dissolved with the aid of another fusion and extraction and the solution added to the filtrate obtained above. The titanate oxide, which is obtained by an acetate precipitation in the presence of a small amount of sulfurous acid (p. 105), is not free from iron. After being ignited and weighed, therefore, the precipitate is redissolved by the method employed on the original sample, and the iron is precipitated by ammonium sulfide in the presence of ammonium tartrate. The ferrous sulfide is converted to ferric oxide,

and the weight of the latter is deducted from that of the impure titanium oxide obtained above (pp. 95 and 98). In like manner the total quantity of iron is determined gravimetrically in a separate portion of the mineral, i.e., by means of the sulfide process.

W. R. Schoeller and A. R. Powell<sup>87</sup> give schemes for the analysis of both rutile and ilmenite, which leave little to be desired from a standpoint of completeness; but, because of the very brief manner in which the procedures are described, it seems doubtful if the inexperienced analyst could follow them with success.

E. Knecht and E. Hibbert<sup>88</sup> determine the titanium and total iron in either rutile or ilmenite by an apparently simple method. Five-tenths gram of rutile or 0.4 gram of ilmenite is fused with potassium hydroxide in a nickel vessel. The cooled melt is treated with water, and, after transferring to a beaker, hydrochloric acid is added in excess. The solution is made up to 250 cc. and an aliquot part of 25 cc. in the case of rutile or 50 cc. in the case of ilmenite is deoxidized with zinc and hydrochloric acid in Hibbert's reduction flask (Figure 20) and the titanium titrated with a standard solution of ferric ammonium sulfate, using potassium thiocyanate as indicator (p. 145), or with methylene blue (p. 147). In another 50 cc. portion of the ilmenite solution the iron is estimated by direct titration with a standardized solution of titanous chloride.<sup>89</sup> On account of the relatively small quantity of iron that occurs in rutile—as compared with ilmenite—it is best to make this determination on a separate portion of the original material. Accordingly a 2-gram sample of the rutile is dissolved and titrated in the manner just given.

#### (\*\*\*\*\*) The Partial Analysis of Titaniferous Iron Ores.

The term "titaniferous iron ore", as used here, is meant to imply those iron ores, especially magnetites, that contain rather small amounts of titanium as compared with straight ilmenite. As stated above (p. 35), however, there is no sharp distinction between titaniferous magnetite and ilmenite, the one passing gradually into the other. Iron ores running low in titanium are less refractory than ilmenite; consequently much (if not all) of the preliminary decomposition may be effected with acids, any unattacked residue being fused with appropriate fluxes for a comparatively short period of time. It is thus possible, without any added inconvenience, to employ a large sample for the determination of such constituents as occur only in small amounts (e.g., phosphorus). In general, then, iron ores that do not carry too great a quantity of titanium permit a somewhat different treatment, especially in the early stages of the analysis, from that usually applied in the case of either rutile or ilmenite.

*Determination of Titanic Oxide and Phosphorus Pentoxide* (Procedure of A. A. Blair).<sup>90</sup> The mutual interference of titanium and phosphorus, each with the determination of the other, has already been mentioned (p. 109).<sup>91</sup> Thus, J. and H. S. Pattinson<sup>92</sup> have shown by actual experiments that the formation of ammonium phosphomolybdate is seriously interfered with by the presence of a titanic salt. Moreover, A. A. Blair,<sup>93</sup> as early as 1878, observed that, when a solution of ferric chloride containing titanic chloride and phosphoric acid is evaporated to dryness, a "compound of titanic acid, phosphoric acid and ferric oxide" is formed, which is insoluble in dilute hydrochloric acid. J. O. Arnold<sup>94</sup> has even taken advantage of this phenomenon, in order to separate all of the titanium from most of the other constituents of the ore, by intentionally adding ammonium phosphate to the solution prior to the evaporation, the titanium being recovered later from the phosphotitanate of iron by suitable means. It is thus evident that for the correct estimation of phosphoric acid in titaniferous substances (and titanium as well by most methods) these two components should be parted as soon as practicable in the course of an analysis. Blair's method for determining both titanium and phosphorus in the same portion of material is somewhat lengthy and entails a good many manipulations. Only an outline of the procedure is given here; for further details the original text should be consulted.<sup>95</sup>

From 5 to 10 grams of the finely ground ore is dissolved in 30 to 60 cc. of concentrated hydrochloric acid. The decomposition is made as nearly complete as possible by the mild application of heat, and the solution is then evaporated to dryness.<sup>96</sup> The residue is digested with 20 to 40 cc. of strong hydrochloric acid until the chlorides have been redissolved, the solution is considerably diluted and filtered through paper, the residue being washed with cold water. The titanium will be found partly in the residue and partly in the filtrate. The residue is dried and ignited in a platinum crucible, treated with 5 to 10 drops of concentrated sulfuric acid and a sufficient quantity of hydrofluoric acid and the acids evaporated off in a radiator—the sulfuric acid being vaporized at the lowest possible temperature (not above 150°C.) so as to avoid loss of phosphoric acid.<sup>97</sup> Meanwhile the filtrate is made nearly neutral with ammonium hydroxide and deoxidized by the addition of ammonium bisulfite. The solution is then acidified with hydrochloric acid (5 cc. of concentrated acid) and the sulfurous acid removed by boiling while a current of carbon dioxide gas is passing through the liquid. A small part of the iron is now reoxidized to the ferric condition by the careful addition of bromine water, or else a little ferric chloride is introduced, and the solution is promptly cooled. Ammonium hydroxide is again added until a close approach to neutrality

is obtained, the stopping point being indicated by the appearance of the precipitate, first white, then red and finally green. A few drops of acetic acid should dissolve the green ferrous hydroxide but leave behind a small quantity of reddish ferric hydroxide. One cc. of acetic acid (sp. gr., 1.04) is added, followed by enough boiling water to bring the volume up to about 480 cc., and the solution is heated rapidly to boiling and maintained in ebullition for 1 minute; whereupon it is filtered rapidly through a large paper and the precipitate washed slightly with hot water. After burning the filter apart from the precipitate, both the ash and the precipitate are united with the residue obtained above, and the whole is fused with sodium carbonate (3 to 5 grams) and a little sodium nitrate. The melt is extracted with hot water, and the residue, which consists chiefly of ferric oxide and sodium titanate, is washed (preferably with a hot 1 or 2 per cent solution of sodium carbonate). To make sure that all of the phosphoric acid has been dissolved out, the fusion and leaching should be repeated.<sup>98</sup>

The residue from this extraction, which contains the titanium, is dissolved by means of a bisulfate (preferably pyrosulfate) fusion, followed by digestion with 5-10 cc. of concentrated sulfuric acid and a suitable amount of water. With the solution occupying a volume of about 400 cc., 50 cc. of a saturated solution of sulfur dioxide, or 5 cc. of ammonium bisulfite,<sup>99</sup> is added; and, after filtering, the titanium is precipitated by hydrolysis of the acetate (cf. p. 92), the solution being rendered as nearly neutral as possible without causing permanent precipitation by the addition of ammonium hydroxide and boiled after the introduction of 20 grams of sodium acetate and one-sixth of the volume of acetic acid (sp. gr., 1.04). The precipitate of titanic acid is collected and washed in the usual manner (p. 92) and ignited to titanic oxide. It should be tested for platinum (derived from the crucible), after redissolution, by the hydrogen sulfide method (p. 163). In the filtrate from the platinum sulfide the titanium is again thrown down by the acetate process exactly as described above, and the weight of the purified oxide is taken as correct.

The filtrate from the residual sodium titanate, etc., as obtained above, will contain all of the phosphoric acid and only a negligible quantity of titanium. It may therefore be used for the determination of this ingredient by any of the well established methods. See C. Baskerville's procedure below (p. 181). Blair's<sup>100</sup> process, wherein the use of the molybdate reagent is avoided, is no longer in accordance with current practice.

Pattinson and Pattinson<sup>101</sup> modify Blair's procedure by reducing the iron completely to the ferrous state, adding a sufficient excess of ammonium aluminum sulfate and precipitating with ammonium hydrox-



ide.<sup>102</sup> In this way aluminum phosphate is thrown down instead of the corresponding iron compound.

N. D. Ridsdale<sup>103</sup> has proposed a new procedure for the determination of phosphorus in titaniferous iron and iron ores, which removes the need for separating the phosphoric acid from titanium by the tedious double fusion with sodium carbonate (p. 179). Four to 6 grams of the sample is treated in the manner already given (p. 178), and that part of the phosphoric acid that remains with the siliceous residue is recovered by evaporating with hydrofluoric and nitric acids, fusing and adding the extract to the main solution. Arsenic, should it happen to be present, may be separated as sulfide after deoxidation of the solution<sup>104</sup> or, if preferred, by volatilization as tribromide or chloride. The basic acetate precipitate, which contains all of the titanium and phosphoric acid and only 0.1 to 0.2 gram of iron, is obtained according to Blair (p. 178). This is dissolved in 25 cc. of warm hydrochloric acid (sp. gr., 1.16) and the solution is diluted to a volume of about 100 cc. Two to 3 cc. of bromine water is added to make sure that the iron is fully oxidized, and the excess of bromine is removed by boiling for 2 or 3 minutes. After cooling the solution to 15°-20°C., the iron and titanium are precipitated by cupferron (p. 90), using 2 or 3 cc. in excess. Ten to 15 cc. of a 6 per cent solution is usually enough. The precipitate is coagulated by shaking for about a minute and then removed by filtration through a 9 cm. paper. The washing is performed by adding nine small portions of a cold mixture (1:9) of hydrochloric acid (sp. gr., 1.16) and water, using in all from 90 to 135 cc. of the washing fluid. Ten cc. of nitric acid is added to the filtrate and the whole is evaporated down to a bulk of 100 cc. Should the solution appear cloudy at this stage, a few cubic centimeters of bromine water are added and the liquid is boiled for a few minutes. A little ferric chloride is added to the still warm solution to serve as an indicator, and then ammonium hydroxide is introduced until the precipitate of ferric hydroxide just makes its appearance; whereupon the liquid is again heated to boiling and cleared by the careful addition of nitric acid. Five cc. of ammonium nitrate (600 grams per liter) is added, the solution brought to the boiling point and then removed from the source of heat and the phosphoric acid precipitated by pouring in 23 cc. of molybdate reagent.<sup>105</sup> After shaking for about 2 minutes, the ammonium phosphomolybdate is given from 2 to 10 minutes to settle, when it is filtered and washed with a 0.1 per cent solution of potassium nitrate in the usual manner. Finally, the precipitate is dissolved in a measured excess of 0.149 N sodium hydroxide and the determination completed by titrating back with nitric acid of the same normality.<sup>106</sup>

*Determination of Phosphorus Pentoxide* (Procedure of C. Baskerville).<sup>107</sup> Two grams of the dried and finely powdered ore is intimately mixed with 20 grams of a flux composed of ten parts of sodium carbonate and one part of potassium nitrate,<sup>108</sup> and the charge is thoroughly fused in a large platinum crucible. The cooled mass is repeatedly boiled with portions of water, and the leachings, which should measure about 300 cc., are filtered, and the insoluble matter is well washed with hot water. Twenty-five cc. of a solution of ferric chloride, containing about 0.1 gram of iron, is introduced, hydrochloric acid is added in excess, the carbon dioxide thus liberated is expelled by boiling and the iron, etc., are precipitated with ammonium hydroxide. The precipitate is filtered off, washed with hot water, which may with advantage contain a little ammonium nitrate, and redissolved in 40 cc. of hot nitric acid (sp. gr., 1.43). After partial neutralization with 25 cc. of strong ammonia solution, the liquid is either heated or cooled to 85° C. and the phosphoric acid thrown out by adding 30 cc. of molybdate reagent. The mixture is shaken vigorously for 5 minutes, the precipitate allowed to settle, separated from the mother liquor by filtration, washed and titrated according to the method of C. E. Manby, as modified by J. O. Handy<sup>109</sup> (i.e., by the alkalimetric method).

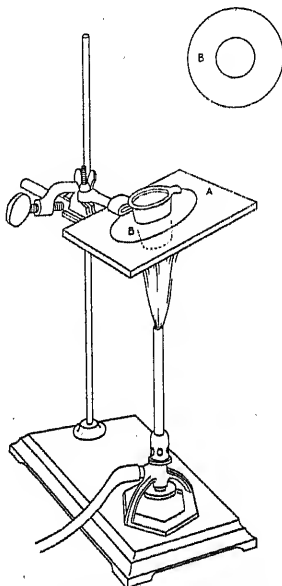
In Baskerville's procedure, as given above, no provision is made for the removal of silicic acid, which is known to interfere with the precipitation of phosphoric acid by ammonium molybdate. In the analysis of materials containing considerable quantities of silicon dioxide, therefore, the extract from the fusion should be acidified with hydrochloric acid and evaporated to dryness so as to render the silicic acid insoluble. The residue is warmed with dilute hydrochloric acid, water is added and the solution filtered. Ferric chloride may now be added and the remainder of the above technique followed without further modification.<sup>110</sup>

The molybdate reagent is prepared as follows: One hundred grams of molybdic anhydride, or 120 grams of 85 per cent molybdic acid, is mixed with 400 cc. of water and 80 cc. of ammonia solution (sp. gr., 0.90) is added. This solution is poured into a mixture of 400 cc. of nitric acid (sp. gr., 1.42) and 600 cc. of water. A small quantity of sodium ammonium phosphate (0.05 gram) is dissolved in a little water and added to the ammonium molybdate solution, which is then thoroughly stirred and set aside for at least 24 hours. After removing the precipitate of ammonium phosphomolybdate by filtration the solution is ready for use. It maintains its strength best when the bottles are kept in a cool dark place.<sup>111</sup>

*Determination of Total Sulfur.* Sulfur may exist in iron ores as sulfides (pyrite, galena, etc.) or as sulfates (gypsum, barite, etc.);<sup>112</sup>

but it is customary to simply determine the total amount of it regardless of the form in which it was originally present.

One gram of the finely powdered ore is thoroughly mixed with 10 grams of sodium carbonate and a small quantity (not more than 0.5 gram) of potassium nitrate in a spacious platinum crucible, and the whole is fused, the crucible being heated carefully at first, but finally at the highest temperature of a Méker burner or blast lamp. To avoid as much as possible contamination of the charge by sulfur compounds



(U. S. Geological Survey, Bull. 700, p. 34, 1919.)

FIG. 25.—W. F. Hillebrand's device for excluding flame gases from the interior of crucibles during ignition. A, asbestos board; B, platinum foil.

from the gas, the crucible should be set snugly in a hole in a slightly inclined asbestos board. See Hillebrand's <sup>118</sup> arrangement (Figure 25). The melt is disintegrated with boiling-hot water, a few drops of alcohol are added to decompose the sodium manganate, the solution is filtered and the residue is washed with a 1 per cent solution of sodium carbonate. The filtrate, occupying a volume of about 150 cc., is made slightly acid with hydrochloric acid, 20 cc. of barium chloride solution (25 grams of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  to the liter) is added drop by drop with constant stirring to the hot liquid, and, after allowing several hours for the precipitate to subside, it is collected on paper and washed with hot water in the usual manner. The barium sulfate is ignited carefully

in a platinum crucible and weighed. It may be tested for silicon dioxide by evaporating with hydrofluoric acid and a drop of sulfuric acid (p. 124) and observing whether or not there is any loss of weight.

The ore may also be opened up by fusion with sodium peroxide in a nickel crucible; but the aqueous extract must be thoroughly boiled before filtering so as to decompose the sodium pertitanate which is soluble in water.<sup>114</sup>

A blank analysis should be made, omitting the potassium nitrate in the first method of fusion for fear of injuring the platinum crucible—there being no oxidizable matter present, and the weight of the barium sulfate found, if any, deducted from that obtained above. If the reagents are free from sulfur, however, the necessity for making this correction may be obviated by using an alcohol lamp<sup>115</sup> or electric furnace.

*Determination of Total Iron Oxides.* From 0.3 to 0.5 gram of the finely ground ore, depending upon the iron content, is treated in a small Pyrex basin with 10 cc. of hydrochloric acid (sp. gr., 1.19), keeping the vessel covered with a watch-glass and warming on the hot plate just below the boiling temperature, until the material seems to suffer no further attack. Thirty cc. of water is then added and the solution is filtered through a small paper, the insoluble residue being transferred completely to the filter and washed several times with small portions of cold water. The residue is ignited in contact with the filter, 1 cc. of sulfuric acid (1:1) and 5 cc. of hydrofluoric acid (48 per cent) are added and the silicon dioxide is removed by evaporating in the nickel crucible radiator (Figure 15) until the sulfuric acid fumes copiously (cf. p. 124). If solution seems to be complete at this point, the syrupy liquid may be diluted with a little water and added to the main portion. If not, nearly all of the sulfuric acid is vaporized in the radiator, and the non-siliceous residue is fused with a small lump of potassium pyrosulfate. The cooled melt is treated in the crucible with 5 cc. of sulfuric acid (1:1) and a like volume of water, warming to effect solution, and this portion is added to the main solution obtained above. The entire solution is now evaporated down in a basin or casserole with the previous addition of 20 cc. of sulfuric acid (1:1) until fumes of sulfur trioxide are freely evolved and it is reasonably certain that all hydrochloric acid has been expelled. After thorough cooling the residual solution is diluted with 40 cc. of water, and the whole is transferred to a 150 cc. flask, using as little water as possible with which to rinse the basin. The iron can now be determined by the method of Gooch and Newton, which is fully described on p. 152 *et seq.* Should the ore contain vanadium, as is often the case, its amount must be otherwise estimated (pp. 164 and 174) and the titer

for iron corrected on the assumption that the vanadium is reduced to the trivalent condition (cf. pp. 163 and 167).

(\*\*\*\*\*) **Other Methods for Assaying Titanium Ores (Rutile, Ilmenite and Titanic Iron)**

*Procedure of J. Waddell.*<sup>116</sup> J. Waddell finds that titanium-bearing iron ores are readily decomposed by fusion with sodium peroxide in an iron crucible, eight times the weight of the sample being a sufficient quantity of the flux. After the disintegration of the mass by water, the solid matter dissolves in sulfuric acid. From this point on the cupferron method (pp. 90, 96 and 163) is followed with but little modification. It is also permissible, after separating the iron as sulfide (p. 96), to determine the titanium colorimetrically, notwithstanding the presence of a little tartaric acid, provided an equal amount be added to the standard (cf. pp. 134 and 135). The latter expedient, however, applies only to ores that contain comparatively little titanium (p. 127).

In this connection it is well to note that certain chemists of the Bureau of Mines<sup>117</sup> have found that both titanium and zirconium ores are very rapidly decomposed by fusion with a flux composed of three parts of sodium hydroxide and one part of sodium peroxide. Three or four parts of this mixture are used for every one part of the ore.

*Procedure of O. L. Barnabey and R. M. Isham.*<sup>118</sup> From 0.2 gram to 0.5 gram of the sample contained in a platinum crucible is moistened with a little water, 5-10 drops of concentrated sulfuric acid and 1 cc. of hydrofluoric acid are added and heat is carefully applied until fumes of sulfur trioxide cease to be evolved. Five to 10 grams of sodium carbonate and a little sodium nitrate are added and the mixture is fused for at least 30 minutes. The melt is leached with hot water, and the washed residue is dissolved in hot hydrochloric acid (sp. gr., 1.11). From now on the analysis is carried out exactly as given on pp. 101-2.

*Procedure of G. S. Jamieson and R. Wrenshall.*<sup>119</sup> Five-tenths gram of the finely pulverized ore is digested on the steam-bath with 25 cc. of concentrated hydrochloric acid till no further action can be observed. About 20 cc. of sulfuric acid (1:2) is now added, the solution is cautiously evaporated down to the fuming point of the less volatile acid and the heating is continued for an hour at a temperature just below boiling. After cooling, 30 cc. of water is added and the solution is warmed until all soluble salts have dissolved. The insoluble matter is removed by filtration and washed three times with very dilute sulfuric acid and then with cold water. Many titaniferous iron ores yield up all their titanium under this treatment; but, unless this has been ascertained for any given type of ore, the insoluble residue should be tested for titanium. The filtrate is diluted to 500 cc. in a volumetric

flask and aliquot parts are taken of such magnitude that the ignited precipitate of titanitic phosphate shall not weigh more than 0.090 gram. Two grams of tartaric acid is added, the solution is made slightly ammoniacal and the iron is precipitated as sulfide (p. 96). The solution is made neutral with hydrochloric acid (1:1) and 15 cc. is added in excess. The iron sulfide dissolves on warming. With materials high in aluminum the amount of hydrochloric acid may have to be increased (cf. p. 106). Twice the above given quantity will do no harm. The titanium is now precipitated and weighed as phosphate (p. 89).

*Procedure of the Metal and Thermit Corporation.*<sup>120</sup> Five-tenths gram of the sample, pulverized to pass a 100-mesh sieve, is fused with 9 grams of potassium pyrosulfate in a porcelain crucible. The cooled melt is treated with water in a casserole, 35 cc. of sulfuric acid (1:1) is added and the solution is evaporated down till the acid begins to fume. After cooling, the strong solution is diluted with water, and the resulting liquid is boiled until as much as possible of the residue has been brought into solution. The siliceous matter is filtered off, washed alternately with hydrochloric acid (1:1) and water and finally, the use of the acid being discontinued, the washing is completed with water alone. The titanium is now determined in the manner given under manganotitanium (p. 205); that is, beginning at the point where the acidity of the solution is reduced by the addition of ammonium hydroxide. This method is intended more particularly for high grade ores, viz., rutile and ilmenite.

*Procedure of A. Ledebur.*<sup>121</sup> A suitable quantity of the ore (1 to 6 grams) is heated in an atmosphere of hydrogen, whereby the iron is reduced to metal. The deoxidized mass is digested in very dilute sulfuric acid (i.e., 1:40), which dissolves most of the iron and leaves behind the titanitic oxide in a somewhat impure condition. The silicon dioxide is removed from this residue by treatment with hydrofluoric acid and a little sulfuric acid (p. 124). It is then fused with potassium bisulfate, the melt dissolved in water, the solution gassed with hydrogen sulfide to reduce any iron that may still be present to its lower valence and the titanium precipitated in the form of titanitic acid by continuous boiling. Further manipulative details and a cut of the apparatus used for the first reduction of the iron are given in Ledebur's<sup>122</sup> manual.

It is a matter of interest to note here that many years ago Smith<sup>123</sup> employed the method of reduction in hydrogen in analyzing a titaniferous iron mineral.

*Procedure of H. L. Wells.*<sup>124</sup> Five grams of very finely ground titanitic iron ore is digested with 50 cc. of concentrated hydrochloric acid in a covered casserole on the steam-bath, adding more acid if necessary, until the ore has been dissolved as far as possible. One hundred cc.

of sulfuric acid (1:1) is added and the solution is evaporated down until the higher boiling acid fumes copiously, this state of affairs being maintained for about 15 minutes. As soon as the material has cooled, about 200 cc. of water is added, and the solution is boiled until the sulfates have completely dissolved. The insoluble matter is removed by filtration, the filtrate being received in a 1000 cc. graduated flask. If the residue is black, it should be subjected to a repetition of the above treatment. If the mineral is not yet fully decomposed, the insoluble residue should be fused with sodium carbonate. The melt is extracted with water, and the solution is evaporated, first to dryness with an excess of hydrochloric acid, and then with sulfuric acid in the manner described above. The flask is filled to the mark with water, and several aliquot parts of 200 cc. each are taken for analysis. In one of these portions the iron is determined by reduction with hydrogen sulfide and titration with potassium permanganate (p. 151) and in another a permanganate titer is obtained by a slight modification of Newton's process (pp. 139-40), which is equivalent to the sum of the titanium and iron.<sup>125</sup> It is now obvious that with these data in hand the amount of titanium in the ore can be calculated.

Instead of carrying out the reduction in a flask, as proposed by Newton, it is doubtless better to employ the reductor, following the technique of G. E. F. Lundell and H. B. Knowles (p. 140 *et seq.*). Due regard must be paid to the possible presence of interfering substances (e.g., vanadium) in all volumetric methods for estimating titanium, however, and such corrective measures adopted as may seem necessary (see p. 144).

*Procedure of R. K. Murphy.*<sup>126</sup> One gram of the finely powdered substance is treated with 50 cc. of concentrated hydrochloric acid in a covered beaker for about 15 minutes at a temperature slightly below boiling, 0.1 gram of potassium chlorate is added and the heating is continued for another period of 15 minutes (or thereabouts). The solution is filtered when cool, and the residue is washed with a little water. The undissolved part is then fused in a nickel crucible with 5 grams of potassium hydroxide and 1 gram of sodium peroxide, raising the temperature slowly until the charge is in a state of calm fusion and then continuing to heat the crucible to dark redness for something like a half hour. After cooling, the melt is slaked, using only a small quantity of water, and about 50 cc. of concentrated hydrochloric acid is added thereto. The filtrate obtained above and this solution are united, and the entire liquid is warmed on the water-bath for approximately 10 minutes; whereupon the clear solution is filtered into a 200 cc. volumetric flask. The residual matter, which consists of silicic acid with some occluded titanous acid, is treated with a few drops each of nitric and sulfuric acids<sup>127</sup> in a platinum crucible, the acids evapo-

rated off, the paper burned and the impure silicon dioxide ignited and weighed. The silicon dioxide is volatilized by treatment with 1-2 cc. of sulfuric acid and 10 cc. of hydrofluoric acid (p. 124),<sup>128</sup> and the non-siliceous residue is weighed on the assumption that it is pure titanic oxide.<sup>129</sup> The rest of the titanium is determined in a 25 cc. aliquot part ( $\frac{1}{8}$ ) of the above solution by a modification of Hibbert's methylene blue process (p. 148).<sup>130</sup>

*Procedure of T. R. Ball and G. McP. Smith.*<sup>131</sup> The finely powdered ore is fused with one part of potassium fluoride and five or six parts of potassium pyrosulfate, as proposed by W. A. Noyes.<sup>132</sup> It is claimed that with this mode of attack titanium-rich minerals are quickly and completely decomposed. The titanium is then determined by reduction with zinc and acid in the separatory funnel with special attachments and subsequent titration with a standard solution of ferric chloride, using potassium thiocyanate as indicator (p. 145).

(\*\*\*\*\*) **Determination of Titanium in Bauxite.**

Bauxite and related minerals, such as gibbsite and laterite, frequently contain very noteworthy amounts of titanium; in fact, it has even been suggested that bauxite may possibly prove to be a commercial source of titanium.<sup>133</sup> The actual percentage, however, is not too great to permit a determination by the colorimetric method.<sup>134</sup>

According to Handy<sup>135</sup> bauxite may be treated in the following way: One and five-tenths gram of the finely powdered sample, which has been dried at 100° C., is digested with 50 cc. of an acid mixture in a porcelain evaporating basin. The mixture of acids consists of 100 cc. of nitric acid (sp. gr., 1.42), 300 cc. of hydrochloric acid (sp. gr., 1.20) and 600 cc. of sulfuric acid (sp. gr., 1.18). The solution is evaporated until fumes of sulfuric acid appear, and then the heating is continued for 15 minutes longer. As soon as cool, the syrupy liquid is diluted with 100 cc. of water, the mixture is stirred and the solution is boiled for 10 minutes. The residual matter, after being collected on paper and washed with cold water, is ignited in a platinum crucible and weighed. The silicon dioxide is expelled by evaporation with 3-4 drops of concentrated sulfuric acid and 5 cc. of hydrofluoric acid (p. 124). The loss in weight represents the total amount of silicon dioxide in the mineral. The silicon-free residue, which may contain some of the titanium, is dissolved with the aid of a bisulfate fusion, and the extract is added to the main solution. The entire solution is now diluted to exactly 300 cc. and three aliquot parts of 100 cc. each are taken for analysis. In one of these the aluminum, iron and titanium are precipitated by ammonium hydroxide in the presence of ammonium chloride. The titanium may be determined in this precipitate by the colorimetric



method (p. 127 *et seq.*) To this end the precipitate may be dissolved in dilute sulfuric acid while still moist, if the other components are not to be estimated, or after ignition by means of a pyrosulfate fusion (see below, p. 192). The other constituents of bauxite are determined by well-known processes.<sup>138</sup>

V. Lenher and W. G. Crawford<sup>137</sup> determine the titanium in bauxite colorimetrically by means of their thymol reagent. Three-tenths gram of the sample is fused with potassium bisulfate. Decomposition is said to be complete in half an hour. The fusion is taken up with concentrated sulfuric acid, and the titanium is estimated according to p. 136.

It is also permissible, after having obtained a sulfuric acid solution by any appropriate procedure, e.g., as in Handy's method, to determine the titanium by the cupferron process (pp. 90, 96 and 107).<sup>138</sup>

**(\*\*\*\*\*) Determination of Titanium in Manganese Ores (Procedure of Booth, Garrett and Blair).<sup>139</sup>**

Two grams of the finely ground ore is boiled with about 20 cc. of concentrated hydrochloric acid till no further action ensues; whereupon the solution is evaporated to dryness. The residue is dissolved (with the aid of a little hydrochloric acid) and the evaporation to dryness is repeated. The salts are taken up with hydrochloric acid, using about 15 cc. of concentrated acid, and the adequately diluted solution is filtered. The siliceous residue is ignited in a platinum crucible, evaporated with hydrofluoric and sulfuric acids (p. 124) and the second residue is likewise ignited. This is fused with a small quantity of sodium carbonate, the melt is dissolved in hydrochloric acid (1:1) and the solution is added to the above filtrate. The solution is now made *very faintly alkaline* with ammonium hydroxide, boiled and filtered. After redissolution in dilute hydrochloric acid the precipitation is repeated. The hydrochloric acid solution of the second precipitate is made nearly neutral with ammonium hydroxide, the iron is reduced with ammonium bisulfite and the aluminum, titanium and phosphoric acid are precipitated with phenylhydrazine (p. 93). This precipitate is ignited in a platinum crucible, fused with potassium pyrosulfate and the titanium is estimated colorimetrically in the sulfuric acid solution by the hydrogen peroxide method (p. 127 *et seq.*).

**(\*\*\*\*\*) Determination of Titanium and Zirconium in Zirconium Ores (Procedure of G. E. F. Lundell and H. B. Knowles).<sup>140</sup>**

The ores of zirconium are baddeleyite and zircon (Table I). A natural mixture of these two, containing about 75 per cent of zirconium dioxide, is imported from Brazil under the trade name of "zirkite."<sup>141</sup>

Four grams of sodium tetraborate (borax) is fused in a platinum crucible. When the flux has become cool, 0.3 gram of the 100-mesh sample is placed on top of it, and the mixture is heated over a Méker burner, stirring occasionally with a stiff platinum wire, until a complete decomposition has been secured, which will normally require not more than half an hour. The wire is removed and placed in a 250 cc. beaker. The melt is made to solidify on the sides as well as on the bottom of the crucible (p. 162); and, when thoroughly cool, both the lid and the crucible are put into the same beaker that contains the wire and covered with 150 cc. of hydrochloric acid (1:5). The beaker is then set on the steam-bath so as to keep the contents warm till solution is complete. The solution is transferred to a platinum basin, 20 cc. of sulfuric acid (1:1) is added and the liquid is evaporated down until fumes of sulfur trioxide escape. After cooling, the volume is made up with water to 100 cc. The impure silicon dioxide is filtered off, washed with hot water and reserved for subsequent treatment. The filtrate and washings are allowed to stand overnight in a warm place to throw down, as zirconium phosphate, interfering amounts of phosphoric acid. If a precipitate forms, it is collected on a filter, washed with ammonium nitrate (5 per cent solution) and reserved. The filtrate and washings from the small precipitate of zirconium phosphate are treated with 5 grams of ammonium chloride and ammonium hydroxide is added in slight excess. After boiling for a minute or two, the solution is filtered and the precipitate is washed with a 2 per cent solution of ammonium nitrate. The filtrate from this precipitate is of no further interest and may therefore be rejected. The precipitate is dissolved in 100 cc. of a hot 5 per cent solution of sulfuric acid, the paper being washed thoroughly with hot water. This paper is ignited, along with those containing the impure silicon dioxide and the zirconium phosphate, in the original platinum crucible. The mass is moistened with a little water, 5 cc. of hydrofluoric acid and 1 cc. of sulfuric acid (1:1) are added and the crucible is heated in a radiator till the sulfuric acid has been completely expelled (p. 124). The non-siliceous matter is fused with a small quantity of sodium carbonate, the melt leached with water, the insoluble residue filtered off and washed with hot water. This residue, consisting of sodium zirconate, etc., is ignited in a platinum crucible, fused with potassium pyrosulfate, the melt dissolved in 5 per cent sulfuric acid and the solution added to the main one obtained above, i.e., to the solution of the ammonium hydroxide precipitate in 5 per cent sulfuric acid. The acidity is reduced to 1 per cent of sulfuric acid by volume, either by dilution or by partial neutralization with ammonium hydroxide, and the solution is gassed with hydrogen sulfide. In case a precipitate of metallic sulfides is produced, it is filtered off and washed with a 1 per

cent sulfuric acid solution saturated with hydrogen sulfide. In the filtrate, which should occupy a volume of about 200 cc., the iron is removed as sulfide (p. 96), after which the titanium and zirconium are co-precipitated by the cupferron reagent (pp. 90 and 98) from a solution containing 10 per cent of sulfuric acid by volume.<sup>142</sup> After weighing, the mixed oxides are fused with potassium pyrosulfate and the melt is dissolved in sulfuric acid (10 per cent by volume). Since the precipitate produced by cupferron may contain rare earths, the solution is diluted to exactly 100 cc. and divided into two 50 cc. portions.

One of the aliquot parts is used for the estimation of titanium. If the amount is small enough, it is determined by Weller's colorimetric method (p. 127 *et seq.*). If, on the other hand, the amount is too large for an exact color comparison, it is best to titrate the titanium with potassium permanganate after the solution has been passed through a reductor in the manner prescribed by Lundell and Knowles (p. 141 *et seq.*).

In the other aliquot the rare earths (including thorium) are determined according to Hillebrand.<sup>143</sup> The solution is treated with potassium hydroxide in excess, and the precipitate is washed once or twice by decantation and then to a slight extent on the filter. The precipitate is transferred to a small platinum dish by means of a fine jet of water, hydrofluoric acid is added and the solution is evaporated to dryness. The residue is extracted with 5 cc. of a 5 per cent solution of hydrofluoric acid. A clear solution at this point establishes the absence of rare earths. The insoluble matter, if there be any, is collected on a small filter supported by a perforated platinum or hard rubber cone and washed with from 5 to 10 cc. of the same hydrofluoric acid. The crude rare earth fluorides are washed into a small platinum dish, the paper burned and its ash added and the whole evaporated to dryness with a little sulfuric acid. The sulfates are dissolved in dilute hydrochloric acid, the rare earths thrown out by ammonium hydroxide, the precipitate collected on a filter, redissolved in hydrochloric acid, the solution evaporated to dryness and the residue treated with 5 cc. of a boiling hot 5 per cent solution of oxalic acid. After 15 minutes the oxalates are collected on a small filter, washed with not more than 20 cc. of a cold 5 per cent solution of oxalic acid and ignited to oxides.<sup>144</sup>

It is now obvious that, if the sum of the rare earth oxides and the titanic oxide be subtracted from the weight of the cupferron precipitate, the difference will be the zirconium oxide.

It may be well to remark here that only about 85 per cent of the rare earths is recovered in the above process. However, since these are usually present in small amount, as compared with the zirconium, the error thrown on that constituent is not apt to be serious.

Brown<sup>145</sup> has worked out an excellent scheme for the analysis of either zircon or baddeleyite, which depends in large measure upon the use of the cupferron reagent. The processes given provide for the estimation of silicon dioxide, total iron, zirconium, titanium, aluminum, manganese and water. Adequate details are included in the original paper.

Still other investigators have studied the analysis of zirconic materials; consequently a variety of methods is available.<sup>146</sup>

(b) Silicates, Titanosilicates, Titaniferous Silicate Rocks, Clays, Sands, Soils, Etc.

(\*) The Analysis of Silicates, Titanosilicates and Titaniferous Silicate Rocks.

*Author's Procedure* (Applicable to Large Amounts of Titanium). One gram of the sample, prepared as described above (p. 158), is mixed with 6 or 7 grams of sodium carbonate in a platinum or palau crucible of not less than 25 cc. capacity (preferably larger). If the rock be decidedly basic, and especially if it contain pyrite, 0.3 gram of potassium nitrate should be added also. The charge is melted very gradually over the Bunsen burner, so as to avoid excessive effervescence, but later on the entire mass is subjected to very thorough fusion with the aid of the Méker burner or blast lamp. The melt is cooled quickly in the manner described under rutile (p. 162). If a palau crucible has been used for the fusion, the dry cake will detach itself almost entirely from the walls of the containing vessel.<sup>147</sup> As much as possible of the cake is transferred to a beaker of Pyrex glass, using hot water and applying a platinum spatula to remove that which adheres to the crucible, the beaker is covered with a watch-glass and about 15 cc. of hydrochloric acid (sp. gr., 1.19) is introduced through the lip opening. The beaker is placed on the water-bath and allowed to remain there until effervescence has ceased and there is no longer any disengagement of chlorine. The contents is then transferred to a 300 cc. platinum basin. Five cc. of the same acid is used to clean the crucible, and this too is poured into the platinum basin. The crucible is then dried at 100°C., and, if any silicic acid remains on its inner surface, it is removed by wiping with moistened bits of ashless filter paper. The solution is evaporated to apparent dryness on the water-bath, the mass is allowed to cool, 15 cc. of concentrated hydrochloric acid is poured in and made to wet the residue thoroughly, an equal volume of water is added and the basin is covered and put back on the water-bath for 10 to 30 minutes. The solution is diluted further, filtered through a 9 cm. paper and the silicic acid is very thoroughly washed with cold water.

The filtrate is returned to the same basin and evaporated again—this time to complete dryness. The residue is moistened with 10 cc. of hydrochloric acid (1:1), and, after standing on the water-bath for about 5 minutes, more water is added (about 40 cc.) and the solution is filtered through a fresh paper. The last trace of silicic acid is wiped out of the basin with small pieces of filter paper, and the residue is, as in the first instance, very thoroughly washed.

The two papers, containing the siliceous residues, are ignited in a tared platinum crucible, the Méker burner or blast lamp being eventually applied for a period of about 30 minutes, i.e., until a constant weight is obtained. The silicon dioxide is then volatilized by evaporation with hydrofluoric and sulfuric acids (p. 124), and the non-siliceous residue is subjected to the high temperature previously employed for about 5 minutes. The loss of weight is silicon dioxide. The material remaining in the crucible consists of the oxides of aluminum, iron, titanium and phosphorus; hence the crucible is put aside (without cleaning) for the ignition of the ammonium hydroxide precipitate.

To the filtrate from the silicic acid, occupying a volume of some 200 cc. in a Pyrex beaker, 10 cc. of hydrochloric acid (sp. gr., 1.19) is added, and the usual double precipitation is made with ammonium hydroxide (p. 168 *et seq.*).<sup>148</sup>

The precipitate, after ignition to constant weight in the reserved crucible, represents the sum total of the aluminum, iron, titanium, phosphoric acid and, should they happen to be present in determinable amounts, the chromium, vanadium and zirconium; but, on the other hand, if the operations have been properly conducted, it will be entirely free from manganese, calcium and magnesium.<sup>149</sup> It is therefore fused with about 7 grams of potassium pyrosulfate, the melt extracted with 10 cc. of concentrated sulfuric acid and a sufficient quantity of water, the small amount of silicon dioxide determined and its weight added to that of the main portion obtained above and the non-siliceous matter brought into solution by means of another fusion and extraction—the two solutions being of course united for the determination of iron and titanium. The above operations are fully described under rutile (p. 161 *et seq.*).

In the sulfuric acid solution of the ammonium hydroxide precipitate, after the removal of the platinum (p. 162), the iron is thrown out as sulfide (p. 96), whence it may be determined either gravimetrically (p. 98) or volumetrically (pp. 150-3), and in the filtrate from the ferrous sulfide the titanium is precipitated with the cupferron reagent (p. 90). The first titanium precipitate is liable to be slightly impure owing to the occlusion of alkalis and possibly vanadium.<sup>150</sup> After taking

a tentative weight, therefore, it is fused with 1 gram of sodium carbonate, the melt extracted with hot water, the residual sodium titanate washed with a hot 2 per cent solution of sodium carbonate, the filter and residue returned to the crucible, the paper burned, the mass fused with another 1 gram portion of sodium carbonate and the fusion dissolved by introducing about 2 cc. of sulfuric acid (sp. gr., 1.84) into the crucible with due regard to the manipulatory precautions given on p. 97. The strong solution is diluted with cold water. If a few flocculent particles of silicic acid make their appearance at this point, the solution should be filtered through a small paper, the residue ignited, the silicon dioxide volatilized (p. 124) and whatever remains brought into solution by fusing with a very small lump (not more than 1 gram) of potassium pyrosulfate and extracting with a little dilute sulfuric acid. By using the fluxes sparingly, as herein indicated, not enough alkali salt will have been introduced into the solution to interfere noticeably with the cupferron process. However, practically all alkali can be removed by a preliminary precipitation with ammonium hydroxide, if so desired. The cupferron precipitation is made as usual in a volume of 400 cc., in which there is also present 40 cc. of sulfuric acid (1:1).

The other constituents of silicate minerals and rocks may be determined according to such methods as are given in well-known treatises on the subject.<sup>151</sup>

*Procedure of W. F. Hillebrand*<sup>152</sup> (Applicable to Small Amounts of Titanium). The technique is practically the same as that given above (p. 191) down to the point of obtaining a sulfuric acid solution of the ammonium hydroxide precipitate. The iron is then determined volumetrically by reduction with hydrogen sulfide and titration with potassium permanganate (p. 151), and in the titrated solution, after reducing the volume by evaporation, the titanium is estimated colorimetrically by the hydrogen peroxide method (p. 127 *et seq.*).

In addition to the above, there is a scheme of analysis due to T. M. Chatard,<sup>153</sup> which is particularly applicable to magnesian silicate rocks, wherein the chromium, titanium, barium and phosphoric acid are determined on the same 2-gram portion of the sample. The silicon dioxide and total iron are estimated in the usual manner (pp. 191 and 193) on 1 gram of the rock powder. Since the titanium is determined gravimetrically by the method of Gooch<sup>154</sup> (in a slightly modified form), the process can be used on rocks that contain large quantities of this element. The original article, which is replete with details, may be consulted for further information. Moreover, Hillebrand<sup>155</sup> gives a condensed and slightly altered description of Chatard's procedure, in which the possible presence of vanadium is provided for.

**(\*\*) The Analysis of Clays.**

The treatment of clays does not differ materially from that of silicate rocks. In specimens that contain comparatively little iron, however, this constituent may with advantage be determined colorimetrically by the thiocyanate process, as J. W. Mellor<sup>156</sup> has shown.

The estimation of titanium in clays, which is best carried out in the colorimetric way, is, according to R. Rieke and R. Betzel,<sup>157</sup> a matter of some importance; since the color of the body after burning depends on the titanium as well as on the iron content, and also on the degree of subdivision of the iron and titanium compounds.

**(\*\*\*) The Analysis of Sands.**

The tendency of titanium minerals to become concentrated in the decomposition products of various rocks has already been emphasized (pp. 22, 28 and 29). Ordinary sands that consist for the most part of quartz, with subordinate amounts of silicate and oxide minerals, do not present any peculiar analytical difficulties. On the other hand, those sands that contain noteworthy amounts of certain rarer minerals (such as chromite, zircon, monazite, etc.) require special treatment.<sup>158</sup> In other words, the chemical analysis of sands in its broadest sense is too complex to justify one in attempting to give general methods.

*Determination of Titanium and Chromium in Beach Sand* (Procedure of E. P. Barrett).<sup>159</sup> Five-tenths to 1 gram of the 150-mesh sample is fused with 6 to 8 grams of sodium peroxide in a porcelain crucible. The melt is leached with 400 cc. of water, boiling for at least 15 minutes. The solution is filtered when cool, and the residue is washed with dilute sodium hydroxide. The chromium may be determined in the filtrate by one or other of the standard methods. The residual matter, which contains all the titanium, is washed through the filter with a hot 10 per cent solution of sulfuric acid, and the paper is cleansed by repeated applications of hot water. Ten cc. of hydrochloric acid is added to the solution, which should now have a volume of about 100 cc. The titanium is determined by the Shimer method (p. 146).

**(\*\*\*\*) The Analysis of Soils.**

A method for the preparation of the soil sample is given by the Association of Official Agricultural Chemists.<sup>160</sup>

*Determination of Water and Titanium* (Procedure of F. P. Dunnington).<sup>161</sup> One gram of the soil is heated to low redness in a platinum crucible, and the loss in weight is reported as "water and organic matter".

The mass is moistened with a little water, 3 or 4 cc. of hydrofluoric acid is added, the liquid is carefully removed by evaporation and the

residue is ignited gently (not above a low red heat). Seven or 8 grams of sodium bisulfate is then introduced, cautiously melted and maintained in a fluid state for 30 or 40 minutes—until a clear yellow melt is obtained. The fusion is cooled, dissolved without heating in 5 per cent sulfuric acid, any remaining silicic acid filtered off and the filtrate and washings received in the 100 cc. comparison tube A (Figure 16). Meanwhile a peroxidized standard solution is prepared according to the directions given on p. 128. In order to correct for the iron in the test solution, it is matched as closely as may be with a little of the standard, the small volume so employed being, of course, deducted before making the calculation for titanium. Hydrogen peroxide is now added to the test, and its color is compared with that of the standard (contained in tube B) in the manner already given (p. 129).

It is of course perfectly feasible to determine the titanium in soils according to the same technique that is used on silicate rocks (p. 193).<sup>102</sup>

### (c) Carbonates (Limestones).

The purer limestones, on being subjected to intense blast ignition for 15 minutes, are rendered completely decomposable by hydrochloric acid. With the more argillaceous varieties, however, the sample should be mixed with half its weight of sodium carbonate and ignited, first over the Bunsen burner and then over the blast lamp, until a thoroughly sintered mass is obtained.<sup>103</sup>

Accordingly, 1 gram of the rock powder, having been treated in either of the above ways, is transferred to a platinum evaporating dish, and slaked with a little water. Twenty cc. of hydrochloric acid (1:1) is then introduced into the dish, and an additional quantity (5 or 10 cc.) of the same acid is used to clean the crucible. The silicic acid is separated by the usual method of double evaporation (p. 191), and in the filtrate, which should occupy a volume of 150 to 200 cc. and contain 10 to 15 cc. of concentrated hydrochloric acid, the iron, aluminum, titanium, etc. are precipitated by the careful addition of ammonium hydroxide in the presence of 1 gram of ammonium persulfate, using five drops of a 0.5 per cent solution of rosolic acid in alcohol (1:1) as indicator.<sup>104</sup> After heating to the boiling point for 1 minute, the precipitate is collected and washed moderately with a hot 2 per cent solution of ammonium chloride. It is then redissolved in hot hydrochloric acid (1:3) and the precipitation is repeated. The ignited and weighed precipitate is redissolved by means of a pyrosulfate fusion (p. 192), and the iron and titanium are determined—the former titrimetrically (p. 151) and the latter colorimetrically (p. 127).



## (d) Columbates and Tantalates.

The analysis of minerals that contain titanium in addition to columbium and tantalum (Table I.) is fraught with countless difficulties. Not only do the acid-earths present a combination of elements that is hard to handle, even when other substances have been removed, but some of the minerals (e.g., hatchettolite) contain also noteworthy amounts of zirconium, thorium, uranium and the rare earths as well as many of the commoner elements. In fact, it must be frankly admitted that such analytical schemes as have been thus far suggested as being applicable to this class of materials leave much to be desired both in point of accuracy and convenience. There is good reason to hope, however, that present-day researches in this field, especially those of Schoeller and his co-workers,<sup>165</sup> will in time evolve processes that are eminently more satisfactory than any that are now known.

High specific gravity on the part of a mineral, provided it does not contain an abnormal amount of iron, may sometimes be taken as indicating the presence of columbium and tantalum. For instance, the specific gravity of strüverite, as determined by Hess and Wells,<sup>166</sup> is 5.25, which is considerably higher than the maximum value for rutile and the average value for ilmenite (see pp. 28 and 29). As a matter of fact, strüverite from the Black Hills of South Dakota contains 34.8 per cent of tantalum oxide and 6.2 per cent of columbium oxide.<sup>167</sup> On the contrary, some of the more complex minerals are even lighter than rutile. Thus two varieties of ellsworthite from Hastings County, Ontario, which were examined by T. L. Walker and A. L. Parsons,<sup>168</sup> showed specific gravities of 3.608 and 3.758 respectively, which, however, must be due, at least in part, to the presence of water (12.22 per cent and 11.42 per cent).

Another fact, which should be borne in mind, is that, although many published analyses of columbite and tantalite do not show the presence of titanium, certain specimens contain this element in very noteworthy amounts.<sup>169</sup>

The following analytical scheme, which has been used by E. W. Todd<sup>170</sup> on Canadian minerals, seems to offer a reasonably good plan to pursue in the chemical examination of this class of materials:

One-half gram of the mineral is fused with potassium pyrosulfate in a platinum crucible, and the melt is thoroughly disintegrated by boiling with 300 cc. of water to which 5 cc. of sulfuric acid has been added. After digesting just below the boiling point so as to settle the precipitate, the solution is filtered and the residue is washed free from acid with hot water. The precipitate contains all of the columbium, tantalum and silicic acid along with a considerable part of the titanium. It is

also contaminated with tin, zirconium, iron and perhaps with aluminum, calcium, uranium and rare earths.

The ignited precipitate is treated with 2 cc. of sulfuric acid and 3 cc. of hydrofluoric acid to expel silicon dioxide (p. 124), and the acid earths are subjected to further purification.

The residue is fused with potassium carbonate without unduly prolonging the time, the mass is leached with 100 cc. of hot water and the precipitate is filtered off and washed. These operations are repeated, using, however, a smaller quantity of potassium carbonate. The combined filtrates, which contain the columbium and tantalum and also some titanium and tin, are acidified with sulfuric acid, boiled for 10 minutes and treated with sulfurous acid. The precipitate is collected on a filter, washed with water, treated on the paper with a warm solution of ammonium sulfide to remove tin and washed again with water. The precipitate is now ignited to constant weight. It still contains a small fraction of the titanium originally present.

The determination of columbium and tantalum in the above precipitate has already been given (pp. 119-20).

The titanium is most readily determined colorimetrically in a separate portion of the mineral powder (p. 127 *et seq.*).<sup>171</sup> Since, however, the greater part of the titanium will have been separated from columbium and tantalum in the above operations, it is permissible to determine this part gravimetrically; consequently, if this be added to the amount that remains with the columbium and tantalum, which is estimated colorimetrically, an independent value for titanium is obtained.

The residue from the potassium carbonate fusions is ignited, fused with potassium pyrosulfate and combined with the filtrates obtained in the purification of the columbium and tantalum. The other constituents of the mineral may then be determined in accordance with known processes.

Certain other investigators, who have had occasion to analyze the titanocolumbates and titanotantalates, have given an account of their methods. Thus F. W. Mar<sup>172</sup> has published his examination of a mineral, which was supposed to be perovskite,<sup>173</sup> from Magnet Cove, Arkansas. Hess and Wells<sup>174</sup> describe the methods employed by them on strüverite. O. Hauser and H. Herzfeld<sup>175</sup> give a scheme for the analysis of blomstrandite. Information may also be obtained from the text of Schoeller and Powell.<sup>176</sup>

#### (e) Phosphates.

The phosphate rocks, such as are used as fertilizers, contain only trifling amounts of titanium,<sup>177</sup> which, as far as the author is aware, has no agricultural significance.

The phosphates of iron, aluminum and titanium may be precipitated together under the conditions laid down by the Fertilizer Division of the American Chemical Society,<sup>178</sup> and the titanium in this precipitate may then be determined colorimetrically with due regard to the interfering action of phosphoric acid (pp. 127, 134 and 135).

The peculiar igneous rock known as "nelsonite", which occurs in the piedmont section of Virginia, contains in some of its phases large amounts of the mineral apatite<sup>179</sup> and the titanium minerals rutile and ilmenite (p. 34). T. L. Watson and S. Taber<sup>180</sup> distinguished six different kinds of nelsonite; hence it is practically impossible to give a general scheme of analysis that would apply to all the varieties of this petrologic type. Specimens that are rich in silicate minerals (hornblende-nelsonite and gabbro-nelsonite), and which contain comparatively little titanium and phosphoric acid, may be analyzed in much the same way as ordinary silicate rocks. Even the usual procedure for separating silicic acid (p. 191 *et seq.*) needs no modification; since Penfield and Foote<sup>181</sup> have shown that the amount of silicon volatilized by small quantities of fluorine in minerals can be safely neglected. On the other hand, those varieties that are practically free from quartz and silicates require a somewhat different treatment. On account of the great difficulty of handling considerable quantities of titanium and phosphoric acid in the same solution (pp. 109 and 178), it is best to dissolve the apatite in dilute hydrochloric acid and then analyze the solution and the residue separately. The solution will contain the phosphoric acid, the calcium and magnesium (of the apatite) and only traces of titanium and iron. The residue may be used for the determination of silicon dioxide, titanium, manganese and magnesium (of the ilmenite). The small amount of titanium that passes into the extract may be estimated colorimetrically in an aliquot part, the two values being combined to make the total, and the remainder of the solution used for the determination of calcium and magnesium. In like manner, another portion of the original material is dissolved in dilute nitric acid in order to have an appropriate solution for the phosphoric acid determination. Still another sample is used for total iron, which is gotten into solution by means of a pyrosulfate fusion—the iron being, of course, estimated volumetrically. Other constituents, such as water, fluorine, sulfur, manganese (if so desired) and ferrous iron,<sup>182</sup> may be determined, each in a separate portion of the rock powder, by appropriate methods. The above outline of methods for analyzing nelsonite is to be taken as merely suggestive. This unusual combination of substances confronts the analyst with a good many difficulties; so much so, in fact, that the matter might well be made the subject of further study.

Certain monazite sands contain titanium owing to an admixture of

titanium minerals (chiefly ilmenite) rather than to the presence of titanium in the monazite crystals themselves. Methods for the analysis of monazite sand are given by C. Glaser<sup>188</sup> and G. Chesneau<sup>189</sup> respectively. If the amount of titanium is not too great to be determined by the colorimetric method, the bleaching action of phosphoric acid on the peroxidized solution should be taken into account (pp. 134 and 135).

#### (f) Ashes of Plants.

Titanium frequently occurs in plants, but it is usually present in excessively small amounts. Improved methods for the analysis of plant ashes are described by W. O. Robinson, L. A. Steinkoenig and C. F. Miller<sup>185</sup> as well as a furnace of special construction for burning away the organic matter.

### (4) ANALYSIS OF COMMERCIAL PRODUCTS.

#### (a) Metals and Alloys (Other than Iron and Steel).

##### (\*) The Analysis of Metallic Titanium.

According to M. A. Hunter<sup>186</sup> the supposedly pure titanium obtained in his process (p. 43) may be analyzed in the following way:

From 0.15 to 0.16 gram of the metal is dissolved by prolonged boiling in moderately concentrated hydrochloric acid, the oxidation completed by adding a drop of nitric acid and the titanium precipitated with ammonium hydroxide (p. 88). In this procedure it is evidently assumed that the absence of iron has been demonstrated by an appropriate qualitative test.<sup>187</sup>

W. G. Mixter<sup>188</sup> analyzes Hunter's material in a somewhat different manner. The sample is dissolved by means of a bisulfate fusion, and the aqueous solution is boiled until the titanium has been completely thrown out in the form of titanous acid (p. 91).

Results obtained by these two methods are in excellent agreement.

##### (\*\*) The Analysis of Titanium Carbide (Procedure of P. W. and E. B. Shimer).<sup>189</sup>

The following procedure was used by Shimer and Shimer with apparent success in analyzing titanium carbide, which had been concentrated from a specimen of "salamander". The salamander, in turn, had been taken from the hearth of a blast furnace in which titaniferous iron ores were being smelted.<sup>190</sup>

*Determination of Titanium.* One-tenth gram of the carbide is dissolved in nitric acid (sp. gr., 1.20), sulfuric acid is added in considerable excess and the solution is evaporated down till fumes of sulfur

trioxide make their appearance—the fuming being continued until it is reasonably certain that all nitric acid has been expelled. The residue is dissolved in hot water, the solution filtered, put through the reductor and the deoxidized solution titrated with ferric ammonium sulfate in the manner already given (p. 146). The titanium value is reported as titanium carbide,  $TiC$ .

Other methods for determining titanium in titanium carbide are given by Shimer.<sup>191</sup>

*Determination of Iron.* A much larger portion of the material is dissolved by the same treatment, and the sulfuric acid solution is reduced with hydrogen sulfide and titrated with potassium permanganate (p. 151).

*Determination of Graphitic Carbon.* A sample of appropriate size, depending upon the amount of insoluble carbon, is treated with nitric acid (sp. gr., 1.20), and the residue is collected on a felt of ignited asbestos in the Shimer filter-tube. The graphite is then burned in a current of oxygen in the Shimer combustion crucible,<sup>192</sup> or quite as well in a boat placed in an electrically heated combustion tube (Figure 26). See below under ferro-titanium (p. 201).<sup>193</sup>

It may be added here that, in accordance with a communication from L. E. Barton,<sup>194</sup> the total amount of carbon in titanium carbide of electric furnace manufacture can be determined by direct combustion. Two-tenths gram of the finely powdered substance is mixed with 2 grams of 100-mesh zircon sand and burned in an "alundum"<sup>195</sup> boat without bed.

*Determination of Siliceous Residue.* A gram or more of the sample is dissolved in nitric acid (sp. gr., 1.20), the solution diluted with water, the insoluble matter collected on a filter, ignited and weighed in the usual manner.

### (\*\*\*) The Analysis of Ferro-Titanium.

*Determination of Silicon, Iron, Titanium and Zirconium* (Author's Procedure). In a covered Pyrex basin 0.75 gram of the finely powdered alloy is treated with a mixture of 20 cc. of sulfuric acid (1:1), 5 cc. of concentrated nitric acid and 10 cc. of concentrated hydrochloric acid—warming until effervescence ceases. The cover glass is removed and the solution evaporated down until fumes of sulfur trioxide appear. The basin is allowed to cool, 60 cc. of water and 10 cc. of concentrated hydrochloric acid are added and the liquid is boiled until the salts have completely dissolved. The solution is filtered through an ashless paper, and the residue, which must be completely transferred to the filter, is washed with hot dilute hydrochloric acid (1:9). The paper with its contents is thoroughly dried in a platinum crucible, the ignition

is made with an abundant supply of air and the carbon-free residue is finally brought to constant weight over a Méker burner. The silicon dioxide is then volatilized by evaporating with 1 cc. of sulfuric acid (1:1) and 5 cc. of hydrofluoric acid (p. 124), the loss in weight multiplied by 0.4676 being equal to the silicon. Any material that remains is dissolved by fusing with a small lump (about 2 grams) of potassium pyrosulfate and extracting with 5 cc. of sulfuric acid (1:1) and enough water to fill the crucible half full, warming gently to aid solution. The two solutions are now combined and the volume is made up to exactly 250 cc. in a carefully calibrated flask, and two portions of 100 cc. each are withdrawn by means of an accurate transfer pipette.

Two and one-half grams of either citric or tartaric acid is added to one of the aliquot parts and the iron is separated by the sulfide process (p. 96). The sulfide precipitate contains all the iron and may therefore be used for the estimation of this constituent (p. 98); but it is perhaps preferable to determine the iron volumetrically in the other 100 cc. portion (p. 150 *et seq.*).

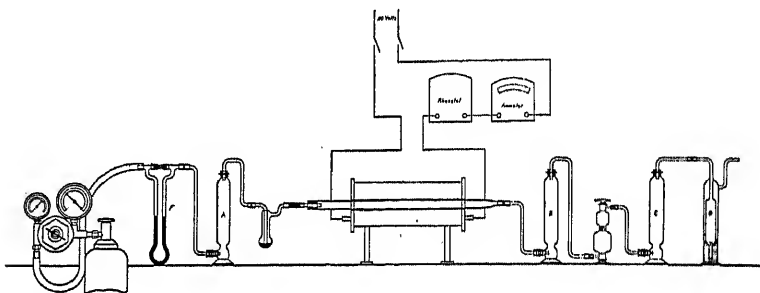
In the filtrate from the ferrous sulfide the titanium is determined by the cupferron method (pp. 90 and 98). Since the one-half factor weight was taken for analysis, every 0.001 gram of titanic oxide corresponds to 0.20 per cent of titanium.<sup>199</sup>

The precipitate produced by cupferron contains the zirconium, should it happen to be present in the alloy, as E. M. Hayden, Jr., and the author<sup>197</sup> have shown. After redissolution, therefore, one may test for zirconium by the phosphate method (p. 112).

*Determination of Carbon.* The carbon in ferro-carbon-titanium, as manufactured by the Titanium Alloy Manufacturing Company, can be completely burned in oxygen at 1000°C. without the aid of any of the so-called "boosters".<sup>198</sup> In like manner, F. Ibbotson<sup>199</sup> states that ferro-titanium is easily decarburized, with or without red lead, by direct combustion in oxygen. C. M. Johnson,<sup>200</sup> on the other hand, considers that, in order to make sure of complete oxidation with all varieties of ferro-titanium, it is safer to employ the red lead flux. Accordingly, from 0.5 to 2 grams of the 30-mesh powder, the actual amount depending upon the probable percentage of carbon (see pp. 70-1), is intimately mixed with 4 grams of red lead, the charge is introduced into a boat of Johnson's clay and the combustion is performed in a tube of the same material.

Descriptions of various "trains" for determining the carbon in metallic products are to be found here and there in the literature. No attempt will be made to give a thorough exposition of the subject of carbon estimation here. In short, then, the author has had very gratifying experiences in using the apparatus of W. R. Fleming<sup>201</sup> with such

minor modifications as are shown in Figure 26. The flow-meter F has been substituted for the pressure gage of Fleming. The author does not know the inventor of this instrument; but it was used a great deal during the recent war in connection with experimental work on gases. The depression of the mercury column in the rear limb is empirically proportional to the rate at which the gas is passing through the capillary tube at the top. Having once calibrated the instrument, therefore, it is a simple matter to ascertain the rate of flow by observing the linear value of the above-mentioned depression. Furthermore, both the



(*Iron Age*, vol. 93, p. 64, 1914.)

FIG. 26.—W. R. Fleming's combustion apparatus (modified) for the rapid determination of carbon in steel.

zinc (sulfur absorbent) and phosphorus pentoxide have been charged into the tower B with an intervening layer of asbestos between the two, thus eliminating one piece from the train. Finally, the tower C, which contains phosphorus pentoxide, has been interposed between the Fleming absorption tube and the gas-washing bottle G to prevent any possible diffusion of moisture from the latter back into the former. The temperature inside the combustion tube is occasionally taken by means of a pyrometer, degrees being plotted against amperes; hence any desired temperature can be maintained through the proper adjustment of the rheostat. The following working conditions have been found satisfactory for a great variety of materials: The combustion tube is heated to about 1050°C., oxygen is fed to the burning metal at the rate of about 300 cc. per minute and the time allowed for the combustion and sweeping is exactly 10 minutes. It is, of course, very important to obtain a constant "blank" before beginning the actual experiments and to deduct this value before calculating the carbon from the weight of carbon dioxide.

*Determination of Phosphorus* (Procedure of the Titanium Alloy Manufacturing Company).<sup>202</sup> Five grams of the sample is digested with 100 cc. of hydrochloric acid (1:1) at the boiling temperature until

the residue undergoes no further attack. The solution is diluted a little and filtered, the insoluble matter being washed with hot water, and the filtrate is placed on the hot plate (or water-bath) so as to evaporate off the greater part of the hydrochloric acid. The residue is calcined in a large platinum crucible, mixed with 10 grams of sodium carbonate and about 0.25 gram of potassium nitrate and thoroughly fused. The melt is digested with hot water and the leachings are filtered. The filtrate is acidified with nitric acid and added to the original solution of the sample, from which most of the hydrochloric acid has been expelled. The composite solution is then evaporated down until salts begin to crystallize out; whereupon 40 cc. of nitric acid (sp. gr., 1.20) is added and the evaporation to the point of incipient crystallization is repeated. Another 40 cc. portion of the same nitric acid is added and the solution is again evaporated until a similar degree of concentration has been reached. After cooling, the solution is made nearly neutral with ammonium hydroxide and the phosphorus is precipitated with the molybdate reagent (p. 181). From this point on the determination is finished as in steel analysis.<sup>203</sup>

*Determination of Sulfur.* The Titanium Alloy Manufacturing Company<sup>202</sup> has in the past determined sulfur in ferro-carbon-titanium by the evolution method.<sup>204</sup> Johnson,<sup>205</sup> however, states that titanium interferes with the evolution process, the results being decidedly too low. Unless it has been proven for any given variety of ferro-titanium that the sulfur is completely disengaged as hydrogen sulfide when the metal is dissolved in hydrochloric acid, it would seem better, therefore, to employ the gravimetric method.

One gram of the powdered alloy is fused with 10 grams of sodium carbonate and 1 gram of sodium nitrate, and the sulfur is determined in the aqueous extract in the ordinary way (p. 182).

Ibbotson,<sup>206</sup> instead of resorting to a fusion, dissolves the alloy in a mixture of hydrochloric acid and potassium chlorate. After boiling off the chlorine, the iron, titanium, etc., are removed by adding ammonium hydroxide.<sup>207</sup> The filtrate is made slightly acid with hydrochloric acid and treated with barium chloride in the usual manner.

*Determination of Manganese.* Manganese is best determined by the sodium bismuthate method (p. 163), using a sulfuric acid solution of the alloy. In case hydrochloric acid has been employed in the preliminary treatment, as for the estimation of silicon, iron and titanium (p. 200), it must be scrupulously removed by evaporating with sulfuric acid in excess and maintaining the latter at its fuming point for some time.

*Determination of Aluminum* (Procedure of C. Grandjean).<sup>208</sup> One gram of the alloy is roasted in a muffle furnace for 15 minutes. It is



then fused in a nickel or silver crucible with 25 to 30 grams of pure sodium hydroxide. The melt is taken up in water, the solution boiled for 5 minutes, filtered and the residue washed thoroughly with hot water containing a little sodium carbonate.<sup>209</sup> The filtrate, on being acidulated with hydrochloric acid, should give no test with hydrogen peroxide, showing the absence of titanium. The solution is then evaporated to dryness so as to render silicic acid insoluble, the residue treated with hydrochloric acid and water and the solution filtered. The aluminum can now be precipitated by the careful addition of ammonium hydroxide to the hot solution (p. 107). The first precipitate is dissolved in hydrochloric acid and the aluminum is thrown out again by the same technique in order to completely remove the sodium salt.

The precipitate should be tested for phosphorus, and, if present, its amount determined and the proper correction applied.

Other methods for determining aluminum in materials containing large amounts of iron and titanium have been suggested on p. 168 *et seq.* See also the analysis of zirconium steel (p. 211).

#### (\*\*\*\*) Other Methods for Determining Titanium in Ferro-Titanium.

*Procedure of the Titanium Alloy Manufacturing Company.*<sup>210</sup> Six-tenths gram (factor weight) of the alloy is dissolved in a porcelain dish in a mixture of 15 cc. of sulfuric acid (1:1), 5 cc. of concentrated nitric acid and 10 cc. of concentrated hydrochloric acid. The solution is evaporated until fumes of sulfuric anhydride are evolved. After cooling, 50 to 60 cc. of water and 5 to 10 cc. of concentrated hydrochloric acid are added, and the liquid is boiled until all soluble matter has been taken up; whereupon the solution is filtered into a large beaker (400 or 600 cc.), and the residue is washed with hot water and dilute hydrochloric acid. The iron and titanium are precipitated in the filtrate by adding ammonium hydroxide in slight excess, the solution is filtered *without boiling* and the precipitate is washed twice on the filter with hot water. The filtrate is rejected. The precipitate is dissolved in a very little dilute hydrochloric acid, and the filter is washed with hot water—the solution and washings being received in the original beaker. The titanium is then precipitated by hydrolysis of the chloride in the presence of sulfurous acid (pp. 91 and 104).

*Procedure of the Metal and Thermit Corporation.*<sup>211</sup> One-half gram of the sample, pulverized to pass a 100-mesh screen, is treated in a casserole with 25 cc. of water and 10 cc. of concentrated hydrochloric acid, the liquid being boiled until the alloy suffers no further attack. Five cc. of concentrated nitric acid and 35 cc. of sulfuric acid (1:1) are then added and the solution is evaporated until the sulfuric acid

fumes. When the contents of the casserole have cooled, about 25 cc. of water is added, and the solution is boiled until all soluble matter has been taken up; when it is filtered, the residue being washed alternately with hydrochloric acid (1:1) and hot water. The filtrate is made alkaline with sodium hydroxide or sodium peroxide, the precipitate coagulated by boiling, filtered on a double paper and washed with water. The hydroxides of iron and titanium are dissolved in hot hydrochloric acid (1:1), the solution is diluted to 300 cc., the acidity is reduced by the addition of ammonium hydroxide (leaving the solution only slightly acid), 100 cc. of sulfurous acid (saturated solution) is added and, after thorough stirring, the liquid is boiled for about 10 minutes, i.e., until the odor of sulfur dioxide is only faintly noticeable. The precipitate is collected on a double quantitative filter, washed with hot water until the washings no longer exhibit the reaction for chlorides (silver nitrate test), ignited and weighed as titanium dioxide (cf. pp. 91 and 104).

*Procedure of P. W. and E. B. Shimer.*<sup>212</sup> The following method was used by Shimer and Shimer on Goldschmidt ferro-titanium:

Three-tenths gram of the sample, crushed to pass through a 40-mesh sieve, is dissolved in dilute sulfuric acid, and the solution is oxidized at the boiling temperature with strong potassium permanganate. The excess of permanganate is reduced with a little ferrous sulfate, and the solution is passed through the reductor. The titanium is then titrated with a standard solution of ferric ammonium sulfate, using potassium thiocyanate as indicator (p. 146).

(\*\*\*\*\*) **Determination of Titanium in Mangano-Titanium (Procedure of the Metal and Thermit Corporation).**<sup>213</sup>

Five-tenths gram of the 100-mesh powder is dissolved in a casserole with 30 cc. of hydrochloric acid (1:1). Five cc. of nitric acid and 35 cc. of sulfuric acid are added, and the solution is evaporated till fumes of sulfur trioxide appear. When thoroughly cool, the liquid is diluted with about 50 cc. of water, and the solution is boiled. The silicic acid is filtered off and washed with hydrochloric acid (1:1) and water. The filtrate is made nearly neutral by the addition of ammonium hydroxide, 100 cc. of sulfurous acid (saturated solution) is added and the solution is boiled until the odor of sulfur dioxide has become faint. The titanic acid is collected on a double filter, washed with hot water until the washings are free from sulfate, dried, ignited and weighed as titanic oxide.

(\*\*\*\*\*) **Determination of Titanium in Cupro-Titanium (Procedure of the Metal and Thermit Corporation).**<sup>214</sup>

The procedure is exactly the same as that used by the Metal and Thermit Corporation on ferro-titanium (p. 204).

## (\*\*\*) Determination of Titanium in Other Alloys.

*Determination of Titanium in Titanium-Aluminum* (Procedure of A. E. Hunt, G. H. Clapp and J. O. Handy).<sup>215</sup> Two grams of the alloy is dissolved in a covered porcelain dish by the gradual addition of 50 cc. of a solution of potassium hydroxide (100 grams in 1000 cc. of water),<sup>216</sup> boiling for 10 minutes to insure a complete decomposition. The solution is diluted to about 125 cc., boiled, filtered as quickly as possible and the residue washed ten times with hot water. The insoluble matter, which contains the titanium and iron and is free from aluminum, is ignited and fused with potassium bisulfate. The melt is extracted with water<sup>217</sup> at 40°C., the solution is filtered, the residue is ignited and treated with hydrofluoric and sulfuric acids to remove silicon dioxide (p. 124), a little bisulfate is again fused in the crucible to recover a possible trace of titanium and the second extract is added to the main solution. Titanic acid is then precipitated by boiling the nearly neutral sulfuric acid solution, keeping it charged with sulfur dioxide (pp. 91 and 104).

It is hardly necessary to say that any of the more modern processes for estimating titanium in the presence of iron (q.v.) could be applied to the above solution instead of using the old sulfate hydrolysis with its obvious disadvantages.

*Determination of Titanium in Ferro-Silicon* (Procedure of E. M. Anger).<sup>218</sup> Five-tenths gram of the finely ground sample is treated in a platinum dish with 10 cc. of concentrated nitric acid. Sulfuric acid (1:1) is also added in amounts as follows: 6 cc. for 25 per cent, 3 cc. for 50 per cent, 2 cc. for 75 per cent and 1.75 cc. for 85 per cent ferro-silicon. As the digestion proceeds, hydrofluoric acid is introduced drop by drop until the decomposition is complete; whereupon the solution is evaporated until fumes of sulfur trioxide come off. The residue is taken up with 10 cc. of hydrochloric acid (1:1) and the solution is filtered. The iron and titanium are reduced by zinc, and the titanium is titrated with a standard solution of ferric ammonium sulfate in the presence of potassium thiocyanate (p. 139 *et seq.*).

*Determination of Titanium in Ferro-Zirconium.* In accordance with recent investigations,<sup>219</sup> the addition of zirconium to steel as an alloying element would seem to be an operation of doubtful value; though it is admitted to exert a purging action similar to that of titanium (cf. p. 69). Moreover, H. W. Gillett and E. L. Mack<sup>220</sup> have shown that other zirconium alloys, viz., zirconium-silicon, zirconium-nickel and zirconium-nickel-silicon, are preferable to ferro-zirconium as a means of introducing the metal. It appears, therefore, that the analysis of ferro-zirconium is a comparatively unimportant matter. However,

A. Réglade, M. Geloso and G. Domont<sup>221</sup> give a scheme for the analysis of this alloy, wherein the estimation of titanium is provided for, which may be consulted for the necessary operative details.

### (b) Iron and Steel.

#### (\*) Preliminary Considerations.

The amount of titanium that is apt to be present in iron or steel of present-day manufacture is quite small enough to be determined by the colorimetric method. Even irons that are spoken of as "titaniferous" do not contain much more than 0.1 per cent of titanium; though irons have been produced in the past from titanium-bearing ores that contained as much as 0.5 per cent of titanium.<sup>222</sup> As already noted (p. 69), steel that has been treated with ferro-titanium under proper conditions retains an extremely small amount of the cleansing element, i.e., having done its work, by far the greater part of the titanium passes out of the metal into the slag. However, small amounts of titanium in ferrous alloys may be determined oxidimetrically, using standard solutions of rather low normality, or even gravimetrically, if a sufficiently large sample be taken for analysis. The chief substances that stand in the way of a correct estimation of the titanium in pig-iron, cast-iron or plain carbon steel are phosphorus, vanadium and iron. Phosphorus interferes more particularly in the gravimetric methods, vanadium in the oxidimetric and iron in the colorimetric. In general, then, two courses are open to the analyst: first, he may dissolve the metal in such solvents as leave all but a negligible trace of titanium behind; or, second, he may dissolve the sample as a whole and then either remove the interfering components of the solution by appropriate methods or make use of empirical compensation—the last expedient being applicable only in the colorimetric process.

#### (\*\*) Determination of Titanium in Pig-Iron and Cast-Iron.

*Procedure of A. A. Blair.*<sup>223</sup> Five grams of the drillings is weighed into a 600 cc. beaker and treated with 80 cc. of nitric acid (sp. gr., 1.20), and, when violent action has ceased, 10 cc. of concentrated hydrochloric acid is added. As soon as effervescence has stopped, the cover glass is removed, the solution is evaporated to dryness and the residue is baked until the ferric nitrate is practically all decomposed. The beaker is set aside to cool; then 30 cc. of concentrated hydrochloric acid is added, warming to dissolve the iron compounds, and the solution is evaporated to dryness. The salts are again taken up with another 30 cc. portion of the same hydrochloric acid, the solution is diluted somewhat and the insoluble matter is collected and washed as for a silicon determination.

From this point on the procedure is the same as that given for the determination of titanic oxide and phosphorus pentoxide in titaniferous iron ores (pp. 178-9).

*Procedure of P. W. and E. B. Shimer.*<sup>224</sup> Five grams of the iron is dissolved in 220 cc. of hydrochloric acid (1:10), and, just before filtering, about 1 cc. of hydrofluoric acid is introduced. The insoluble residue is collected and washed in the usual manner; whereupon it is ignited in a platinum crucible until the graphite has been burned off. The filtrate contains no titanium and may therefore be rejected. Should the iron contain vanadium, it is removed as follows: The residue is transferred as completely as possible to a sheet of glazed paper, mixed with a flux composed of equal parts of sodium carbonate and sulfur and the charge is fused for 30 minutes in a porcelain crucible. The crucible is prepared for use by melting a little sugar or tar in it, running the liquid up around the sides and finally igniting with the lid on. The carbon-coating thus produced prevents the flux from attacking the glaze of the crucible. The melt is extracted with hot water, and the solution is filtered. The residue contains the titanium and the filtrate the vanadium (cf. p. 110). As much of the residue as possible is dissolved by treating it on the filter with dilute sulfuric acid. The remainder is ignited in a platinum crucible, fused with potassium bisulfate and a little sodium fluoride and the melt extracted with dilute sulfuric acid. The two solutions are united, boiled to expell hydrogen sulfide, put through the reductor and the titanium titrated with ferric ammonium sulfate (p. 146).

*Procedure of the Bureau of Standards.*<sup>225</sup> Five grams of the sample is dissolved in 40 cc. of hydrochloric acid (sp. gr., 1.05). The insoluble residue, which contains all except a negligible amount of the titanium, is collected on a filter, washed with water and ignited in a platinum crucible. The silicon dioxide is removed by evaporating with hydrofluoric and sulfuric acids (p. 124), the non-volatile matter is fused with sodium carbonate, the melt leached with water, the solution filtered and the residual sodium titanate, etc. dissolved in sulfuric acid. As the solution always contains a little iron, ferric sulfate is added to the standard titanium solution until the two solutions exhibit the same tint when they are both at the same dilution. The solutions are then peroxidized and compared in a colorimeter (p. 127 *et seq.*).

### (\*\*\*) Determination of Titanium in Plain Carbon Steel.

*Procedure of the Titanium Alloy Manufacturing Company.*<sup>226</sup> A standard titanium solution is first prepared by dissolving 0.25 gram of a carefully analyzed specimen of carbon-free ferro-titanium, containing about 20 per cent of titanium, in 30 cc. of sulfuric acid (1:3),

oxidizing (when solution is complete) with the least possible quantity of concentrated nitric acid, boiling for a few minutes and diluting the cool solution to such a volume that 1 cc. shall contain 0.0005 gram of titanium. When using a 5-gram sample, therefore, each cubic centimeter of the standard solution represents 0.01 per cent of titanium in the steel. But, since this solution is too strong for most work, it is diluted ten-fold just before making a determination; consequently each cubic centimeter will then contain 0.00005 gram of titanium, which is equivalent to 0.001 per cent of titanium in the steel, assuming that 5 grams has been taken for analysis.

In the case of steel that has been treated with ferro-carbon-titanium all but a trace of the remaining titanium will be found in the residue insoluble in hydrochloric acid.

To determine the titanium, then, 5 grams of the sample is dissolved in 100 cc. of hydrochloric acid (1:1), boiling for a short time. The solution is diluted a little, the insoluble matter is collected on a filter and it is ignited *gently* to destroy carbonaceous material. The residue in the platinum crucible is treated with 3 cc. of sulfuric acid (1:1), 3 cc. of hydrofluoric acid and a few drops of nitric acid, the crucible being carefully heated (p. 124) until copious fumes of sulfuric anhydride make their appearance. After cooling, the residue is taken up by adding a few cubic centimeters of water and boiling. The contents of the crucible is now transferred to a Nessler jar and diluted with cold water to the 50 cc. graduation mark, and the companion jar is filled with water nearly (but not quite) to the corresponding mark. If the test solution is colored slightly yellow by iron, the liquid in the other tube is brought to the same tint by adding dropwise a solution of ferric sulfate. Two cc. of the hydrogen peroxide solution (p. 226) is introduced into each of the comparison tubes; when the operator can judge (from the depth of color that immediately develops in the test solution) whether one or more cubic centimeters of the stronger standard solution is required. Having added the indicated quantity of the stronger standard, the decimally related solution is run in from an accurate burette until an exact agreement in color is reached. The percentage of titanium can now be readily calculated.

F. P. Dunnington's colorimeter (Figure 16) is suitable for the above comparison.

If so desired, the very small amount of titanium that passes into solution as a result of the above treatment may be recovered and determined colorimetrically. This is done by intentionally adding a little potassium aluminum sulfate (ordinary alum) and then precipitating aluminum hydroxide by the phenylhydrazine method (cf. p. 93). The aluminum precipitate collects the trace of titanium and carries it down.

This precipitate is ignited, redissolved and the titanium in the sulfuric acid solution estimated in the manner just given. Since the test solution is apt to have a greenish-yellow color, both ferric sulfate and copper sulfate are used in matching the tint prior to the peroxidization; thereafter the determination is completed in accordance with the above technique. For further details see W. W. Scott's Standard Methods of Chemical Analysis.<sup>227</sup>

*Procedures of C. R. McCabe.*<sup>228</sup> Procedure No. 1 (Titanium above 0.02 Per Cent). Two grams each of the titanium steel and of a similar steel that contains no titanium are treated with 80 cc. of sulfuric acid (1:3) in 300 cc. Erlenmeyer flasks, heating on the hot plate till solution is complete. Four cc. of nitric acid (sp. gr., 1.20) is added to each and the solutions are boiled till fumes cease to be evolved. When cool, the solutions are transferred to comparison tubes, and the two volumes are made equal. They should exhibit the same color at this point. If not, a part of the titanium-free solution, which must be the stronger in iron, is withdrawn. Two cc. of a 3 per cent solution of hydrogen peroxide is then introduced, and, after mixing, enough of a standard solution of titanous sulfate is added to the solution of the non-titanium steel to equal the color of the test, adding water to the test so as to restore the equality of volume in case more than 2 or 3 cc. of the standard is required.

Procedure No. 2 (Titanium below 0.02 Per Cent). Two grams samples of the two different kinds of steel are dissolved in dishes in 50 cc. of concentrated hydrochloric acid. Four cc. of nitric acid (sp. gr., 1.20) is added to oxidize the iron, and, as soon as effervescence is over, the solutions are evaporated to about 10 cc., transferred to separatory funnels and the dishes rinsed with hydrochloric acid (2:1). With the volumes at 25 cc., as much of the iron as possible is removed by one shaking with 50 cc. of ether (free from alcohol), the aqueous layers being drawn off into 400 cc. beakers (p. 100). It is important to manipulate the two solutions in exactly the same way so that the amounts of iron remaining may be equal in the two cases. The solutions are diluted with 225 cc. of hot water, made slightly alkaline with ammonium hydroxide and the precipitates are coagulated by boiling. The solutions are filtered through 11 cm. papers, and the precipitates are washed with hot water till free from chlorides. The precipitates are redissolved in 10 cc. of sulfuric acid (1:3), and the resulting solutions are filtered into 30 cc. comparison tubes. The two solutions should now occupy the same volume, which may vary from 15 to 18 cc. Three cc. of hydrogen peroxide (3 per cent solution) is added to each tube and the comparison is made exactly as described in Procedure No. 1.

It is claimed that by this method as little as 0.001 per cent of titanium in a steel may be detected with perfect certainty.

(\*\*\*\*) **The Analysis of Zirconium Steel** (Procedure of G. E. F. Lundell and H. B. Knowles).<sup>229</sup>

As already indicated (p. 206), zirconium steels will probably not prove to be materials of practical value. However, a method for the analysis of these steels has been very carefully worked out by Lundell and Knowles at the Bureau of Standards. Their process is given here; since it embodies principles that are more than likely to be applicable in other connections.

*Determination of Silicon, Aluminum, Titanium and Zirconium.* Five grams of the steel is dissolved in 50 cc. of hydrochloric acid (sp. gr., 1.20) with mild application of heat and the addition of 1 cc. portions of nitric acid from time to time to insure the complete solution of the zirconium and titanium as well as the oxidation of the iron. The solution is evaporated to dryness, the residue taken up with 10 cc. of hydrochloric acid (sp. gr., 1.20), the solution evaporated to dryness a second time and the residue baked in order to decompose nitrates. After cooling, the more or less basic salts are dissolved in 50 cc. of hydrochloric acid (1:1), the solution is filtered and the insoluble matter is washed with hot 3 per cent hydrochloric acid. The siliceous residue is ignited in a platinum crucible, treated with 1 cc. of sulfuric acid (1:1) and a sufficient quantity of hydrofluoric acid and the silicon dioxide removed by vaporization in the usual manner (p. 124). The silicon can now be calculated from the loss in weight. The small amount of non-volatile residue is gotten into solution by fusing with a little potassium pyrosulfate and dissolving the melt in 10 to 20 cc. of 5 per cent sulfuric acid. This solution is added to the aqueous extract from the ether separation (see below).

The filtrate from the silicic acid is evaporated down to a syrupy consistency, taken up with 40 cc. of hydrochloric acid (sp. gr., 1.10) and extracted with ether (p. 100).<sup>230</sup> The aqueous solution contains a relatively small part of the iron and all of the zirconium, titanium, aluminum, nickel, chromium, etc. It is boiled gently to expell the ether, the solution containing matter recovered from the silicon dioxide is added, a little nitric acid is introduced to make sure that the iron is in the ferric condition and the volume is made up with water to 300 cc. A 20 per cent solution of sodium hydroxide<sup>231</sup> is added, using 10 cc. in excess. The precipitate is filtered off, dissolved in warm hydrochloric acid (1:1) and the sodium hydroxide precipitation repeated. The two alkaline filtrates, which together contain all of the aluminum, are combined. The second precipitate is dissolved in hydrochloric acid (1:1);



and, in order to make certain that any zirconium in the form of its phosphate is completely recovered, the filter paper that formerly contained the precipitate is ignited in platinum, the ash fused with sodium carbonate, the melt leached with hot water, the residual sodium zirconate dissolved in hot hydrochloric acid (1:1) and the solution added to the main one, which contains the greater part of the zirconium and also the titanium.

In the absence of chromium and uranium the aluminum is determined in accordance with the following technique: The alkaline solution, as obtained above, is neutralized with hydrochloric acid, using methyl red as the indicator, and 4 cc. of concentrated hydrochloric acid is added for every 100 cc. of the solution. The aluminum is then thrown out by the cautious addition of ammonium hydroxide (cf. p. 107, continuing the ebullition for 3 minutes after the introduction of the reagent and then setting the beaker aside for 10 minutes. If a precipitate forms, it must be freed from phosphoric acid. Accordingly, it is filtered off (but not washed), and dissolved in warm hydrochloric acid (1:1). The solution is diluted to 50 cc., made alkaline with ammonium hydroxide, neutralized with nitric acid and 2 cc. of the same acid added in excess. With the solution at 50°C. the phosphoric acid is precipitated with the molybdate reagent in the ordinary manner.<sup>232</sup> The ammonium phosphomolybdate is removed by filtration and washed with ammonium acid sulfate.<sup>238</sup> The aluminum is precipitated in the filtrate as directed above, filtered without washing, dissolved in hydrochloric acid (1:1), reprecipitated, filtered, washed slightly with a 2 per cent solution of ammonium chloride and ignited in a platinum crucible. Since the precipitate may occlude some silicic acid, it is treated with hydrofluoric and sulphuric acids; after which it is brought to constant weight by blast ignition.

In the presence of chromium the procedure is the same until the filtrate from the molybdate precipitate has been obtained; whereupon the solution is made ammoniacal, oxidized with a little bromine water, made faintly acid with nitric acid (1:2), ammonium hydroxide added in slight excess, the solution heated to boiling, filtered, the precipitate dissolved in dilute hydrochloric acid and the determination completed in the manner given above.

In the presence of uranium the only modification that it is necessary to make is the substitution of ammonium carbonate for ammonium hydroxide as the final precipitant for aluminum.

In the presence of vanadium the aluminum hydroxide is contaminated with this constituent to a certain extent. The weighed precipitate, therefore, is fused with potassium pyrosulfate, the melt dissolved in 5 per cent sulfuric acid, the solution passed through a Jones reductor into

ferric sulfate and the bivalent vanadium titrated with potassium permanganate (cf. p. 140 *et seq.*). The vanadium is calculated as pentoxide and deducted from the weight of the precipitate in order to arrive at the true amount of aluminum oxide.

The hydrochloric acid solution containing the zirconium and titanium is diluted to 250 cc., partially neutralized with ammonium hydroxide so that every 100 cc. shall contain 5 cc. of concentrated hydrochloric acid, 2 grams of tartaric acid added and hydrogen sulfide passed in until the iron has all been reduced to the ferrous condition. If metallic sulfides appear at this stage, they are removed by filtration. Ammonium hydroxide is added in distinct excess, and the solution is gassed again with hydrogen sulfide—this time for a period of 5 minutes. The precipitate is filtered off and washed with water containing both ammonium sulfide and ammonium chloride (cf. p. 96).<sup>284</sup> The filtrate is neutralized with sulfuric acid, 30 cc. of concentrated acid is added in excess and the volume is made up with water to 300 cc. The solution is digested on the steam-bath until sulfur (and possibly sulfides) have coagulated, filtered, the residual matter washed with 10 per cent sulfuric acid (by volume), the filtrate chilled in an ice bath and the zirconium and titanium precipitated by the cupferron method (p. 90).

The weighed precipitate is fused with potassium pyrosulfate, the melt dissolved in 50 cc. of sulfuric acid (1:9) and the titanium determined either colorimetrically (p. 127) or oxidimetrically (p. 140) depending upon its amount. The zirconium can then be obtained by difference.

### (c) Slags and Refractories.

#### (\*) Determination of Titanium in Slags (Particularly Blast Furnace Slags) (Procedure of Booth, Garrett and Blair).<sup>285</sup>

Two or more grams of the finely ground slag, depending upon the amount of titanium expected, is treated with hydrofluoric acid and a few drops of sulfuric acid in a large platinum crucible, the solution evaporated to dryness and the residue ignited (cf. p. 124).<sup>286</sup> The non-volatile residue is fused with potassium bisulfate, the melt cooled, 4 to 5 cc. of concentrated sulfuric acid is added and the crucible heated again until its contents becomes liquid. The fusion, after thorough cooling, is dissolved in 100 to 200 cc. of cold water in a 600 cc. beaker. The solution should be perfectly clear. Ten to 15 cc. of hydrochloric acid is introduced to increase the color of the ferric iron, the solution is deoxidized with ammonium bisulfite, ammonium hydroxide is added until a permanent precipitate is formed and the precipitate is dissolved in the least possible amount of dilute sulfuric acid. More than enough sodium acetate to react with the sulfuric acid is then stirred in, 30 per

cent acetic acid is added to the extent of one-sixth of the volume and the solution is boiled to precipitate titanous acid. The first precipitate is ignited in the original crucible, redissolved by means of a bisulfate fusion and the titanium thrown down again in accordance with the above technique. The second precipitate should be free from aluminum and iron (cf. p. 178).<sup>237</sup>

If the precipitate is a very small one, it is well to redissolve it with the aid of a bisulfate fusion and determine the titanium colorimetrically (p. 127 *et seq.*).

### (\*\*) The Analysis of Refractory Materials.

The general run of refractory materials may be analyzed in much the same way as silicate rocks (q.v.). The American Society for Testing Materials,<sup>238</sup> however, instead of determining both iron and titanium in the entire solution of the ammonium hydroxide precipitate, as is the usual practice (p. 193), divides it into two aliquot parts. In one of these (1/5) the titanium is estimated and in the other (4/5) the iron. This mode of procedure is obviously less accurate.

In the same article<sup>239</sup> the determination of titanium in chrome ores and chrome brick is provided for.

The estimation of titanium and zirconium in high grade zirconium ores has already been given (p. 188).

### (d) Salts.

There is very little in the literature on the analysis of such water-soluble titanium salts as are used in the textile and leather industries (p. 74).

O. Schütte<sup>240</sup> states that the titanium in the double oxalate of potassium and titanium,  $K_2TiO(CO_2)_2 \cdot 2H_2O$ , can be quantitatively precipitated by ammonium hydroxide. This, of course, presupposes the absence of other substances, such as iron, aluminum, etc., that are precipitable by the same reagent. In like manner, the precipitating function of cupferron is independent of oxalic acid, as it is of many other organic compounds.<sup>241</sup> The oxalate radical may be estimated by titration with a standard solution of potassium permanganate (p. 141).

Knecht and Hibbert<sup>242</sup> analyze titanous chloride, which is obtainable in the market in the form of a strong solution (15 to 20 per cent), in the following manner: A 10-gram sample is diluted to 1000 cc., and an aliquot part of 25 cc. is reduced with zinc and hydrochloric acid in Hibbert's flask (Figure 20) and titrated with ferric ammonium sulfate (pp. 145 and 147). This gives the total amount of titanium. Another 25 cc. portion is titrated in the same way but without prior reduction,

which, of course, gives the titanium in the titanous condition only. The titanous titanium can now be calculated.

I. M. Kolthoff and O. Tomiček<sup>243</sup> find that iron is a very common impurity in commercial preparations of titanous chloride. They test for iron by boiling a portion of the solution with nitric acid and then adding either potassium ferrocyanide (p. 57) or potassium thiocyanate. With the latter reagent the depth of color is proportional to the amount of iron present. They also determine the iron quantitatively by potentiometric titration with potassium dichromate.

The iron in titanous sulfate can be readily estimated by Newton's method (p. 152).

#### (e) Pigments and Paints.

##### (\*) The Analysis of Titanium Pigments (Procedure of the American Society for Testing Materials).<sup>244</sup>

*Physical Examination.* On the determination of specific gravity, color, color strength and coarse particles see the original article.<sup>245</sup>

*Qualitative Analysis.* About 0.5 gram of the sample is placed in a 250 cc. beaker of Pyrex glass, 20 cc. of concentrated sulfuric acid and 7 to 8 grams of ammonium sulfate are added, the materials thoroughly mixed and the liquid boiled for a few minutes. The pigment should dissolve completely; a residue denotes silicon dioxide or siliceous matter of some kind. When the solution has cooled, it is diluted with 100 cc. of water, heated to boiling, allowed to settle, filtered, the residue washed with hot 5 per cent sulfuric acid till free from titanium and tested for lead, etc. The filtrate is examined by the usual methods of qualitative analysis as to whether it contains calcium, zinc, iron, chromium, etc., or not. A portion of the filtrate may be tested for iron by the sulfide-tartrate method (p. 96), warming at the side of the steam-bath to complete the precipitation. Failure to obtain a dark turbidity indicates not only the absence of iron but of nickel, cobalt, lead, copper, etc., as well. If a black precipitate is obtained that dissolves readily in hydrochloric acid, it is probably sulfide of iron. Titanium may be identified by the hydrogen peroxide test (p. 61) or by reduction with zinc or tin (p. 59). The material should also show negative tests for sulfur in the form of sulfides, carbonates and appreciable amounts of water-soluble matter.

*Determination of Water.* Moisture is determined by drying a 1-gram sample for 2 hours at 105 to 110°C. and noting the loss of weight.

*Determination of Water-Soluble Matter.* Two and five-tenths grams of the pigment is placed in a 250 cc. volumetric flask, 100 cc. of water is added and the liquid is boiled for 5 minutes. When the solution has

cooled to room temperature, the flask is filled to the mark with water, the contents mixed and allowed to settle. The supernatant liquid is poured through a dry paper, and, having discarded the first 20 cc., a 100 cc. portion is evaporated to dryness in a tared dish, the residue heated for 1 hour at 105 to 110°C., cooled and weighed.

*Determination of Titanium Dioxide.* Five-tenths gram of the dried sample is dissolved in the manner given under qualitative analysis. The residual barium sulfate, however, is washed with cold 5 per cent (by volume) sulfuric acid. The filtrate is diluted to 200 cc., about 10 cc. of ammonium hydroxide (sp. gr., 0.90) is added to lower the acidity to approximately 5 per cent of sulfuric acid by volume and the titanium is determined volumetrically according to the technique of Lundell and Knowles (p. 140 *et seq.*).

*Determination of Barium Sulfate.* The insoluble residue obtained in the determination of titanic oxide is ignited in a platinum crucible and weighed as barium sulfate. Should there be evidence that this precipitate is contaminated, it may be purified by appropriate methods (see p. 220).

*Determination of Ferric Oxide.* The first prerequisite for this determination is a standard solution of ferric sulfate containing 0.00001 gram of iron in every cubic centimeter. This may be conveniently obtained by standardizing the solution prepared as described on p. 142 by any accurate method, e.g., by means of the reductor,<sup>240</sup> and then diluting it to the desired strength.

One gram of the sample is dissolved as for titanic oxide. The solution along with the suspended barium sulfate is transferred to a 200 cc. graduated flask and the deficiency in volume is made up with water, both liquids being at the room temperature. The solution is passed through a dry filter, the first 20 cc. is rejected and then 50 cc. of the clear filtrate is transferred to a 100 cc. comparison tube. One-tenth N potassium permanaganate is added drop by drop until a pink color pervades the solution and persists for at least 5 minutes. Ten cc. of potassium thiocyanate (2 per cent solution) is then introduced, the volume is made up to 100 cc. and the contents of the tube are thoroughly mixed. The color is at once compared with that of a series of standards.<sup>247</sup> The standards are prepared from the known solution of ferric sulfate (see above) so as to have a range of from 0.000005 gram of iron to 0.00004 gram of iron (0.5 to 4.0 cc.). The desired volumes of the ferric salt solution are delivered into 100 cc. Nessler jars, which already contain 50 cc. of an acid solution (made by dissolving 8 grams of ammonium sulfate in water, adding 20 cc. of concentrated sulfuric acid, cooling and diluting with water to 200 cc.), a few drops of permanganate are added as before and the color is developed with 10 cc.

of the thiocyanate solution. Finally, the standards are diluted with water to 100 cc. and thoroughly mixed.

When only one sample is to be analyzed, it is more convenient to add the standard ferric sulfate from a burette to 50 cc. of the solution containing ammonium sulfate and sulfuric acid (see above), to which also a drop of the permanganate and 10 cc. of the thiocyanate have been added, until the color matches that of the test solution. Enough water should of course be added to the standard to make the final volume practically 100 cc. (cf. pp. 209 and 210).

*Calculations.* The iron is calculated and reported as ferric oxide. This value is multiplied by the factor 1.003 and the product is subtracted from the result for titanium obtained volumetrically in order to arrive at the true amount of titanic oxide. All results should be reported on the dry basis.

#### (\*\*) Other Methods for Analyzing Titanium Pigments.

*Procedure of the Titanium Pigment Company, Inc.*<sup>248</sup> *Determination of Barium Sulphate.* A 0.5 gram sample is dissolved in the manner given above for the determination of titanium dioxide and barium sulfate (p. 216) except that 7 or 8 grams of sodium sulfate is used instead of ammonium sulfate. The residual barium sulfate is collected on a filter, washed with 5 per cent sulfuric acid, ignited and weighed.

*Determination of Titanium Dioxide.* The filtrate from the barium sulfate is subjected to the action of the reductor, and the titanous sulfate is titrated with a standard solution of ferric ammonium sulfate (p. 146).

The ferric salt solution is prepared by dissolving 30 grams of the alum in 300 cc. of water, acidifying with 10 cc. of sulfuric acid, adding potassium permanganate drop by drop as long as the pink color disappears and finally diluting to 1000 cc.

The titanium may also be determined gravimetrically in accordance with the following technique:<sup>249</sup> Five-tenths gram of the pigment is dissolved as directed above, and in the filtrate from the barium sulfate the titanium is precipitated by ammonium hydroxide and redissolved with hydrochloric acid (1:1). The precipitation and redissolution are repeated so as to obtain a solution perfectly free from sulfates. Titanic acid is then thrown out by the method of Baskerville (pp. 91, 104 and 204).

Should the results for titanium obtained by the gravimetric method be higher than those gotten volumetrically, the discrepancy may be due to the presence of zirconium in the pigment. The ignited and weighed

precipitate may, therefore, be redissolved and tested for zirconium by the phosphate method (p. 112).

*Procedure of W. J. Brown*<sup>250</sup> (*National Lead Company*). This method differs chiefly from that adopted by the American Society for Testing Materials in that the receiver is charged with an accurately measured volume of potassium permanganate instead of with an indefinite excess of ferric sulfate. More than enough of a solution of ferrous sulfate to reduce the remaining permanganate is then added and the surplus is titrated with the same permanganate (about 0.1 N).

The potassium permanganate is standardized as usual against sodium oxalate (p. 141), and the ferrous sulfate is titrated with the permanganate at the time of experiment. When operating in this way the "blank" is considerably larger than when ferric sulfate is used as the fixing agent.

*Procedure of A. Eibner*.<sup>251</sup> The analysis of titanium pigment ("titanweiss"), more particularly the Norwegian product (p. 67), is given brief treatment by A. Eibner in Lunge-Berl.: *Chemisch-technische Untersuchungsmethoden*. The proposed methods embody a few qualitative tests and the quantitative determination of the titanium by the Gooch method (p. 106), in which titanous acid is precipitated free from zinc.<sup>252</sup>

(\*\*\*) **The Analysis of Outside White Titanium-Zinc Paint (Semipaste and Ready-Mixed).**

*Procedure of the United States Government*.<sup>253</sup>

*Sampling.* See the original article.

**Laboratory Examination of Semipaste.**

*Physical Examination.* On the examination of the paint as to caking in container, weight per gallon, mixing with linseed oil, color and coarse particles and skins see the original article.

*Determination of Moisture and Other Volatile Matter.* From 3 to 5 grams of the paste is accurately weighed into a flat-bottomed dish (about 5 cm. in diameter), and the sample is spread over the bottom. The vessel with its contents is then heated for 1 hour at 105 to 110°C., cooled and weighed. The loss in weight represents the moisture and other volatile matter.

*Determination of the Total Amount of Pigment.* About 15 grams of the paste (weighed with exactness) is placed in a tared centrifuge tube. Twenty to 30 cc. of "extraction mixture"<sup>254</sup> is added, the charge is thoroughly mixed with a glass rod, which is then removed and washed with some of the extraction mixture, and finally enough more

of the reagent is introduced to make a total of 60 cc. in the tube. The tube is placed in the container of a centrifuge, surrounded with water and the container of the opposite arm is counterbalanced with a similar tube or a tube with water. The tubes are whirled at a moderate speed until the solid matter has settled out completely. The clear supernatant liquid is decanted, the extraction is repeated twice with 40 cc. portions of the same solvent and then once with 40 cc. of ether. After drawing off the ether, the tube is set in a beaker of water at about 80°C. (or on top of a warm oven) for 10 minutes, and then it is placed in a drying oven maintained at a temperature of 105 to 110°C. and allowed to remain there for 2 hours. It is then cooled and weighed. The percentage of pigment may now be calculated.

Having thus obtained a specimen of the pigment, it is ground to a fine powder, passed through a No. 80 sieve to remove any skins, and preserved in a stoppered bottle.

*Preparation of the Fatty Acids.* About 25 grams of the paste is mixed with 15 cc. of aqueous sodium hydroxide<sup>255</sup> and 75 cc. of ethyl alcohol in a porcelain casserole, and the vessel is placed on the steam-bath and heated uncovered until saponification is complete, which will require about 1 hour. One hundred cc. of water is added, the solution boiled, sulfuric acid (sp. gr., 1.20) introduced, using 8 to 10 cc. in excess, the liquid boiled again, stirred and transferred to a separatory funnel, which already contains some water. As much as possible of the aqueous layer is drawn off, the fatty layer is washed once with water and 50 cc. of water and 50 cc. of ether are added. The mixture is shaken very gently with a whirling motion to dissolve the fatty acids in the ether, but not so violently as to form an emulsion. The aqueous layer is run off, and the ethereal solution is washed first with a 15 cc. portion of water and then with successive 5 cc. portions until free from sulfuric acid. The ether solution is transferred to a dry flask, 25 to 50 grams of anhydrous sodium sulfate is added and the flask is stoppered and allowed to stand with occasional shaking at a temperature below 25°C. until the water has been completely removed, which will be shown by the solution becoming perfectly clear above the solid sodium sulfate. The liquid is decanted (if necessary, through a dry filter paper) into a dry 100 cc. Erlenmeyer flask. A rapid current of air, dried by passing through a calcium chloride tower, is led into the flask, which is heated to a temperature below 75°C. by means of a hot plate, until the ether is entirely expelled.

The fatty acids prepared in this way should be kept in a stoppered flask and examined at once.

*Test for Mineral Oil and Other Unsaponifiable Matter.* Ten drops of the fatty acid, as obtained above, are introduced into a 50 cc. test-



tube, 5 cc. of alcoholic sodium hydroxide<sup>256</sup> is added and the liquid is boiled vigorously for 5 minutes. Forty cc. of water is then added, and the solution is well mixed. A clear solution indicates that not more than traces of unsaponifiable matter are present. If, on the other hand, the solution is turbid, the oil is not pure linseed.

*Determination of the Iodine Number of the Fatty Acids.* About 0.15 gram (0.10 to 0.20 gram) of the fatty acids (see above) is introduced into a 500 cc. bottle having a tight fitting glass stopper,<sup>257</sup> 10 cc. of chloroform is added and the bottle is given a rotary motion to dissolve the sample. Ten cc. of chloroform is likewise added to each of two bottles similar to that used in the actual test. Twenty-five cc. of the Hanus solution<sup>258</sup> is next introduced into each of the three bottles, which are then allowed to stand with occasional shaking for 30 minutes. Ten cc. of a 15 per cent solution of potassium iodide and 100 cc. of water are then added, and the iodine is titrated with a 0.1 N solution of sodium thiosulfate, using starch as indicator. From the difference between the average of the two blank titers and the titer obtained on the sample the iodine number of the fatty acids may be calculated.<sup>259</sup>

If the iodine number is less than 170, the oil does not meet the specification.

The standard solution of sodium thiosulfate is prepared in the usual manner and standardized against resublimed iodine.<sup>260</sup>

*Analysis of the Pigment.* The qualitative analysis, determination of water-soluble matter and determination of titanic oxide have already been described (p. 215 *et seq.*).

The ignited and weighed residue of barium sulfate (p. 216) is fused with ten times its weight of sodium carbonate in a platinum crucible for a period of 1 hour. The melt is extracted with 100 cc. of hot water, the solution filtered off and the insoluble matter washed with hot water till free from sulfates. The residual barium carbonate is dissolved in hydrochloric acid (1:1), and, with the solution at the boiling temperature and occupying a volume of about 400 cc., the barium is thrown down as sulfate by adding 10 to 15 cc. of sulfuric acid (1:3).<sup>261</sup> The precipitate is collected on asbestos in a perforated crucible, washed with hot water, ignited and weighed.

On subtracting this result from the weight of the crude barium sulfate the amount of siliceous material is obtained.

Zinc oxide is determined in 0.5 gram of the pigment. The sample is dissolved in 30 cc. of hydrochloric acid (1:2) in a 400 cc. beaker by boiling for 2 or 3 minutes, and the solution is diluted with 200 cc. of water. Ammonium hydroxide (sp. gr., 0.90) is added until the solution reacts slightly alkaline, it is then made just acid again with hydrochloric acid and 3 cc. of concentrated hydrochloric acid is added in

excess. The solution is now heated nearly to the boiling point and titrated with a standard solution of potassium ferrocyanide, using uranyl nitrate (5 per cent solution) as indicator.

The potassium ferrocyanide solution is prepared by dissolving 22 grams of the pure salt in water and diluting to 1000 cc. It is standardized empirically against pure metallic zinc<sup>202</sup> or pure zinc oxide that has been recently ignited.

About 0.2 gram of zinc is dissolved in 30 cc. of hydrochloric acid (1:2) in a 400 cc. beaker. The acidity is adjusted in the manner given above, and the volume is made up to about 250 cc. The ferrocyanide is then run slowly into the hot solution until a drop, when taken out and touched on a drop of the indicator on a white surface, shows an incipient brown color after standing for 1 minute. The end-point should be corrected according to a blank titration in both the standardization and actual analysis. Moreover, it is important that the standardization be performed under as nearly as possible the same conditions of temperature, volume and acidity as prevail in the titration of the sample.

*Calculations.* In case the percentage of barium sulfate is not more than 3.17 times as great as the percentage of titanium oxide (see above), the two are added together and the sum is reported as the percentage of titanium pigment. If the percentage of barium sulfate is greater than this amount, 3.17 times the percentage of titanium oxide is taken as the percentage of barium sulfate to be included in the percentage of titanium pigment and the remainder is included in the percentage of extending pigments. The sum of the percentage of titanium pigment, zinc oxide and water-soluble matter is subtracted from 100 and the remainder is reported as the percentage of extending pigments.

### Laboratory Examination of Ready-Mixed Paint.

*Physical Examination.* On the examination of the paint as to caking in container, weight per gallon, brushing properties and time of drying, resistance to sulphide fumes, color and coarse particles and skins see the original article.<sup>203</sup>

*Determination of Water.* One-hundred grams of the paint is mixed in a 250 or 300 cc. flask with 75 c. c. of toluene, and 50 cc. is distilled over into a graduate. At this point the temperature in the flask should be about 105 to 110°C. The number of cubic centimeters of water that is collected beneath the toluene in the receiver is the percentage of water in the paint.

*Determination of Volatile Thinner.* The moisture and other volatile matter are determined in accordance with the technique given on p. 218, the result is corrected for water (see above) and the remainder is reported as volatile thinner.

*Determination of the Total Amount of Pigment.* The procedure is the same as that given above (p. 218).

*Testing Nonvolatile Vehicle.* The procedures are the same as those given under preparation of fatty acids (p. 219), test for mineral oil and other unsaponifiable matter (p. 219) and determination of iodine number of the fatty acids (p. 219) except that in the preparation of the fatty acids the mixture of paint and alkali is heated on the steam-bath until all volatile thinner has been driven off.

*Analysis of the Pigment.* The procedure is the same as that given above (p. 220).

## PART III.

### REAGENTS.

#### Chapter X.

#### The Preparation of Certain Reagents.

##### (1) GRAVIMETRIC REAGENTS.

##### (a) Ammonium Hydroxide.

Instead of purchasing ammonia water in bottles, which is always more or less impure owing to foreign matter being taken into solution from the glass, it is far better to prepare ammonia solutions in small quantities as needed by passing the gas from a cylinder of liquid ammonia<sup>1</sup> into pure water. E. T. Allen and J. Johnston<sup>2</sup> have shown that when ammonium hydroxide is kept in bottles of ordinary glass it becomes contaminated at nearly twice the rate that it does in bottles of Jena glass, and that in bottles of ceresin (such as are used for hydrofluoric acid) there is no contamination at all. The following simple method of preparing the solution has been used by the author for some time with satisfactory results:

The gaseous ammonia is first bubbled through a little water in a Drexel bottle and then it is passed into a Jena bottle, which contains distilled water to the extent of about two-thirds of its capacity. The Jena bottle is set in a stoneware jar, and the intervening space is packed with cracked ice. The gas stream is continued until a portion, on being taken out and tested with a hydrometer, shows that the desired strength has been attained.<sup>3</sup> If the ammonia solution is to be kept for any considerable length of time, it should be transferred to ceresin bottles.<sup>4</sup>

In case the ammonia solution is going to be used for separating the alkaline earths from other elements, it should be free from ammonium carbonate. The water used to absorb the ammonia, therefore, is subjected to a preliminary boiling while a current of air, which has been

deprived of its carbon dioxide by passage through a soda-lime tower, is being drawn through it. The ammonia is passed through two Drexel bottles: the first contains a fairly strong solution of barium hydroxide and the second pure water.

Having thus prepared the pure ammonium hydroxide, one may, of course, use it to make certain pure ammonium salts. For example, it may be mixed with redistilled acetic acid in the proper proportion to make pure ammonium acetate.

**(b) Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron").**

Nitrosophenylhydroxylamine was first synthesized by A. Wohl<sup>6</sup> in 1894. The ammonium salt of nitrosophenylhydroxylamine was introduced into analytical chemistry by O. Baudisch<sup>6</sup> in 1909 (see pp. 58 and 90). It is easily prepared on a small scale by following the directions of Baudisch.

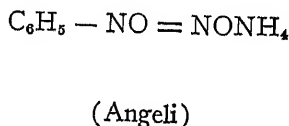
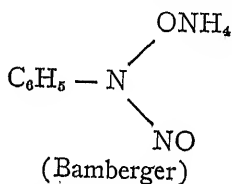
Sixty grams of nitrobenzene, 1000 cc. of water and 30 grams of ammonium chloride are stirred rapidly to an emulsion. Eighty grams of zinc dust is added in small portions to the stirred emulsion by means of a knife blade, the temperature being kept between 16 and 18°C. by the occasional addition of a little shaved ice, until there is no longer an odor of nitrobenzene and the precipitate is gray. The reduction is accomplished in about 30 minutes. The solution is filtered from the zinc hydroxide, which is washed a few times with iced water. The filtrate, cooled to nearly 0°C., is saturated with sodium chloride; whereupon phenylhydroxylamine crystallizes out in white needles. These are collected in a perforated funnel and dried by being pressed between sheets of filter paper. The yield is generally 70 to 80 per cent of the theoretical.<sup>7</sup> The crystals are dissolved in 300 to 500 cc. of commercial ether, and the solution is filtered from any residual sodium chloride. The ethereal solution, cooled to 0°C., is saturated with dry ammonia gas. With the solution still at 0°C., the calculated weight of fresh amyl nitrite (one molecule to every molecule of nitrobenzene) is introduced. The vessel is immediately filled with glistening white crystals of the ammonium salt of nitrosophenylhydroxylamine. After filtration and washing with ether, the crystals are dried by filter paper, and preserved in a closely stoppered bottle in which is also placed a small lump of ammonium carbonate.<sup>8</sup>

The preparation of cupferron has been subjected to detailed study by C. S. Marvel and O. Kamm,<sup>9</sup> who give directions for making the substance in much larger quantity. In fact, they start with 500 grams of nitrobenzene and employ the various reagents in about the propor-

tions given above. D. R. Kasanof <sup>10</sup> states that poor yields of the intermediate product are probably due to a thin coating of zinc oxide on the particles of zinc, and that good yields may be obtained with certainty by first amalgamating the zinc dust. W. K. Slater <sup>11</sup> uses methyl nitrite instead of amyl nitrite for introducing the nitroso group.

Cupferron of reasonably good quality can be purchased in the American market.<sup>12</sup> Some specimens, however, have been observed to contain an undue amount of resinous matter. Others have been actually adulterated with ammonium carbonate.

There seems to be some doubt in regard to the constitution of the ammonium salt of nitrosophenylhydroxylamine; since two formulas occur in the literature, which may be designated the Bamberger and Angeli formulas respectively:



Cupferron is a white crystalline compound, melting at 162°C., easily soluble in water, slightly so in alcohol and insoluble in ether. It crystallizes in silvery plates from hot alcohol containing a little gaseous ammonia. It decomposes slowly when exposed to air and strong light, becoming first yellow and then brown in color and giving off a pungent smell which recalls the odor of nitrosobenzene. The disintegration, however, is greatly retarded by the vapor of ammonium carbonate (p. 224). Old specimens of cupferron may be used in analytical work, provided the decomposition has not gone too far.

The reagent is prepared for use by simply dissolving the compound in cold water and filtering. A 6 per cent solution is the customary strength; but the author has of late employed a 4 per cent solution on titanium.

The ammonium radical of cupferron is replaceable by metals, forming various salts of nitrosophenylhydroxylamine. These derivatives are remarkably stable—some of them, at least, having been obtained as crystalline compounds of definite chemical composition.<sup>13</sup> By properly controlling the acidity of the menstruum it is possible to precipitate certain metals and leave others in solution, thus effecting many cleancut and useful separations (cf. p. 58). The precipitate containing any given metal is always ignited, more or less directly, to the oxide.

## (2) COLORIMETRIC REAGENTS.

## (a) Hydrogen Peroxide.

The interfering action of fluorine compounds in the colorimetric estimation of titanium has already been mentioned (p. 135). W. F. Hillebrand<sup>14</sup> gives a method for testing the reagent for this impurity. Whether or not any of the substances that are commonly present in commercial preparations of hydrogen peroxide, some of which are intentionally added either to retard the decomposition of the solution (the so-called "inhibitors") or to increase its antiseptic properties, exert any deleterious influence on the color test for titanium does not seem to be definitely known; but in all probability the effect is not serious.

L. E. Barton<sup>15</sup> prepares a solution of hydrogen peroxide by dissolving 4 grams of sodium peroxide in 125 cc. of sulfuric acid (1:3) and diluting to 500 cc. The small quantity of sodium sulfate thus introduced is not enough to exert any bleaching action on the color of the peroxidized titanium solution.<sup>16</sup>

F. O. Rice<sup>17</sup> and some of his pupils (M. L. Kilpatrick and O. M. Reiff); in connection with a somewhat extended investigation on hydrogen peroxide, find that a very pure peroxide of almost any desired strength can be prepared by following a comparatively simple procedure. The method follows:

Sodium peroxide is added in small portions to 20 per cent sulfuric acid without allowing the temperature of the solution to rise above 20°C. (ice-bath) until an amount equivalent to 95 per cent of the sulfuric acid has been introduced. After standing for an hour, the hydrated sodium sulfate is filtered off, the crystals washed with cold water and the filtrate distilled in vacuo at 60-65°C. The solution is admitted to the distilling flask in 100 cc. portions by means of a tap funnel, a fresh portion being added whenever the sodium sulfate in the flask appears dry. Finally, when the entire solution has been distilled, the temperature is raised to 85°C. in order to drive over any hydrogen peroxide that may be combined with the sodium sulfate. The distillate is collected in two receivers, the second being cooled to a lower temperature than the first. In the first receiving flask there condenses a rather concentrated hydrogen peroxide (over 20 per cent); in the second a much more dilute (less than 3 per cent). The small amount of chloride that the distillate is almost sure to contain may be removed by treatment with silver sulfate and repeating the distillation in vacuo. The stronger solution may be concentrated further (up to nearly 90 per cent), if so desired, by placing it in a vacuum desiccator over sulfuric acid. Test experiments by Rice and co-workers show that the

yields of hydrogen peroxide obtained in this method of preparation are excellent.

### (b) Dihydroxymaleic Acid.

Dihydroxymaleic acid, which has been used to some extent for the colorimetric estimation of titanium (p. 137), may be prepared in accordance with the method of H. J. H. Fenton,<sup>18</sup> which consists briefly in oxidizing tartaric acid with hydrogen peroxide in the presence of ferrous tartrate. For further details the original article should be consulted.

## (3) OXIDIMETRIC REAGENTS.

### (a) Potassium Permanganate.

Potassium permanganate, when used in volumetric analysis, should be as free from chlorine compounds (and other impurities) as possible. The author has found the brand that is sold under the general designation "Baker's Analyzed Chemicals" and also marked "special" to be a very satisfactory article.<sup>19</sup>

### (b) Ferric Ammonium Sulfate.

Ferric ammonium sulfate, as obtained in the market, may contain traces of iron in the ferrous condition. Even if this is not the case, the salt may undergo reduction in solution because of organic matter in the distilled water or from exposure to sunlight. A permanent 0.05 N solution may be prepared in the following way:

Twenty-four to 25 grams of the crystallized salt is dissolved in water, 30 cc. of concentrated sulfuric acid is added and the volume is made up to 1000 cc. Potassium permanganate (0.05 N solution) is then added dropwise until a permanent pink color pervades the entire liquid. The solution is boiled for about 10 minutes, thoroughly cooled and filtered through an ignited felt of asbestos directly into the storage bottle. It may then be standardized by the reductor method (p. 140 *et seq.*).<sup>20</sup>

### (c) Methylene Blue.

There are two varieties of methylene blue, viz., the hydrochloride,  $C_{16}H_{18}N_3S \cdot Cl \cdot 3H_2O$ , and the zinc chloride double salt,  $(C_{16}H_{18}N_3S \cdot Cl)_2 \cdot ZnCl_2 \cdot H_2O$ . The former, which is also called "medicinal" methylene blue, is the kind that is always used in volumetric analysis. F. W. Attack<sup>21</sup> mentions the occasional presence of a reddish-violet substance, which is not readily reduced, and consequently gives rise to an indefinite end-point. The author, however, has never observed this behavior on



the part of specimens of medicinal methylene blue that had been obtained from reputable dealers.

(4) FLUXES.

(a) Potassium Pyrosulfate.

The pyrosulfates of the alkali metals are preferable to the corresponding bisulfates for opening up minerals, redissolving residues, etc.; since, in using the former, there is no danger of loss by spattering.

Potassium pyrosulfate is prepared by melting together chemically equivalent quantities of potassium sulfate and concentrated sulfuric acid in a spacious platinum dish, stirring occasionally with a platinum rod, until a calm fusion is obtained and steam bubbles cease to form at the bottom of the vessel.<sup>22</sup> The melt is cooled quickly by placing the dish on a clean slab of steel, the cake is broken into pieces the size of hazelnuts with the aid of a pestle and the salt is preserved in a bottle with close fitting glass stopper.

## PART IV.

### NOTES AND REFERENCES.

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- <sup>108</sup> Ruff, O., and Eisner, F.: *Ber.*, **38**, 742 (1905); **41**, 2250 (1908).
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- <sup>111</sup> Gooch, F. A.: *loc. cit.*, p. 436, *ref. 92*.
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## CHAPTER IV

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- <sup>4</sup> Rossi, A. J., and Barton, L. E.: U. S. 1,106,409, Aug. 11, 1914; 1,106,410, Aug. 11, 1914; 1,171,542, Feb. 15, 1916.
- <sup>5</sup> Barton, L. E.: *ibid.*, 1,205,144, Nov. 21, 1916; 1,206,798, Dec. 5, 1916; 1,428,914, Apr. 24, 1917; 1,236,655, Aug. 14, 1917; 1,240,405, Sept. 18, 1917; 1,409,648, Mar. 14, 1922.
- <sup>6</sup> Ilmenite from Pablo Beach, Fla., is being used at the present time.
- <sup>7</sup> "Niter cake" is essentially sodium bisulfate.
- <sup>8</sup> The word "dissolve" is used somewhat loosely here in that titanous sulfate is not very soluble in strong sulfuric acid. It is correct, however, in the sense that a water soluble product is formed.
- <sup>9</sup> Jehsen, G.: *loc. cit.*, *ref. 3*.
- <sup>10</sup> Washburn, W. F.: U. S., 1,412,027, Apr. 4, 1922.
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- <sup>18</sup> Stoughton, B.: *Railway Age Gaz.*, **54**, 245 (1913).
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- <sup>23</sup> Metal and Thermit Corporation, 120 Broadway, New York, N. Y.
- <sup>24</sup> Patents covering ferro-titanium are as follows: Goldschmidt, H., and Weil, O.: U. S., 1,075,782, Oct. 14, 1913; 1,136,670, Apr. 20, 1915.
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- <sup>28</sup> Anon.: Nat. Cannery Assn., Bull. 22-L, 126 (1923).
- <sup>29</sup> Anderson, R. J.: *loc. cit.*, *ref.* 26.
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- <sup>32</sup> Gillett, H. W., and Mack, E. L.: Trans. Am. Electrochem. Soc., 43, 231 (1923).
- <sup>33</sup> Rossi, A. J.: U. S., 700,244, May 20, 1902; 12,764, Mar. 17, 1908; 1,022,599, Apr. 9, 1912; 1,022,595, Apr. 9, 1912; 1,023,331, Apr. 16, 1912.
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- <sup>78</sup> Pick, J.: Mediz. Klinik, (1911) 4033; Remington, J. P., and co-editors: U. S. Dispensatory, 1918, p. 1644. J. B. Lippincott Company.
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- <sup>81</sup> Peacock, S.: *ibid.*, 995,897, June 20, 1911.
- <sup>82</sup> Anderson, R. J.: loc. cit., p. 2, *ref.* 26.

## CHAPTER V

<sup>1</sup> The washing should be performed with a hot 2% solution of sodium carbonate to guard against turbid runnings.

<sup>2</sup> Moses, A. J., and Parsons, C. L.: Elements of Mineralogy, Crystallography and Blowpipe Analysis, 1907, p. 126. D. Van Nostrand Company.

<sup>3</sup> There should be no odor of hydrofluoric acid after the liquid has cooled below the fuming point of sulfuric acid, but is still warm.

<sup>4</sup> Jamieson, G. S., and Wrenshall, R.: J. Ind. Eng. Chem., 6, 203 (1914).

<sup>5</sup> Camp, J. M.: The Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Alloy Steels, 1921, p. 5. Carnegie Steel Company, Pittsburgh, Pa.

<sup>6</sup> Designated the "aluminum and iron groups" by Noyes, A. A., Bray, W. C., and Spear, E. B.: J. Am. Chem. Soc., 30, 481 (1908). Some works on qualita-

tive analysis (e.g., Gooch, F. A., and Browning, P. E.: *Outlines of Qualitative Chemical Analysis*, 1911, p. 41 *et seq.* John Wiley & Sons) divide these elements into two groups, viz., those precipitated by ammonium hydroxide alone (or by the basic acetate process) and those subsequently thrown out by ammonium sulfide.

<sup>7</sup> Noyes, A. A., and Bray, W. C.: *J. Am. Chem. Soc.*, 29, 137 (1907).

<sup>8</sup> It is not permissible to use a solution of ammonium sulfide containing polysulfides because of its solvent action on nickel.

<sup>9</sup> Noyes, A. A., Bray, W. C., and Spear, E. B.: *loc. cit.*, p. 481 *et seq.*, *ref.* 6.

<sup>10</sup> Browning, P. E., Simpson, G. S., and Porter, L. E.: *Am. J. Sci.*, (4) 42, 106 (1916).

<sup>11</sup> Noyes, A. A.: *Tech. Quart.*, 16, 93 (1903); 17, 214 (1904).

<sup>12</sup> Noyes, A. A., and Bray, W. C.: *Chem. Rev.*, 1, 277 (1924). Other articles on qualitative analysis by A. A. Noyes and his co-workers are: Bray, W. C.: *J. Am. Chem. Soc.*, 31, 611 (1909); Noyes, A. A.: *ibid.*, 34, 609 (1912).

## CHAPTER VI

<sup>1</sup> Throughout the description of gravimetric processes, unless otherwise specified, the titanium is understood to be present in the quadrivalent condition.

<sup>2</sup> The preparation of pure ammonium hydroxide will be given in Part III.

<sup>3</sup> Bornemann, K., and Schirmeister, H.: *Metallurgie*, 7, 711 (1910).

<sup>4</sup> Van Brunt, C.: *J. Am. Chem. Soc.*, 36, 1426 (1914).

<sup>5</sup> Merz, V.: *J. prakt. Chem.*, 99, 157 (1866).

<sup>6</sup> Gooch, F. A.: *Proc. Am. Acad. Arts Sci.*, n. s., 12, 435 (1885).

<sup>7</sup> Lundell, G. E. F., and Knowles, H. B.: *J. Ind. Eng. Chem.*, 14, 1136 (1922).

<sup>8</sup> Ericson, E. J.: *Iron Age*, 72, 4 (Aug. 27, 1903).

<sup>9</sup> Jamieson, G. S., and Wrenshall, R.: *J. Ind. Eng. Chem.*, 6, 203 (1914).

<sup>10</sup> E. J. Ericson's formula,  $Ti_2P_2O_8$ , from which he claims to have calculated the above factor, could have no real existence; since it would mean that the titanium is present in the trivalent state, which is quite incompatible with the experimental conditions.

<sup>11</sup> In the absence of iron the sulfur dioxide could probably be omitted.

<sup>12</sup> Baudisch, O.: *Chem.-Ztg.*, 33, 1298 (1909); 35, 913 (1911); Baudisch, O., and King, V. L.: *J. Ind. Eng. Chem.*, 3, 629 (1911).

<sup>13</sup> July, 1925.

<sup>14</sup> Schröder, K.: *Z. anorg. Chem.*, 72, 89 (1911).

<sup>15</sup> Bellucci, I., and Grassi, L.: *Gazz. chim. ital.*, 43, I, 570 (1913).

<sup>16</sup> Thornton, W. M., Jr.: *Am. J. Sci.*, (4) 37, 173, 407 (1914).

<sup>17</sup> Lundell, G. E. F., and Knowles, H. B.: *J. Ind. Eng. Chem.*, 12, 344 (1920).

<sup>18</sup> Lundell, G. E. F., and Knowles, H. B.: *loc. cit.*, *ref.* 17.

<sup>19</sup> Schleicher & Schüll's No. 589 "blue ribbon" filter is satisfactory for the purpose.

<sup>20</sup> Cf. Hillebrand, W. F.: *U. S. Geol. Survey, Bull.* 422, 138 (1916); *Bull.* 700, 154 (1919).

<sup>21</sup> Bettel, W.: *Chem. News*, 28, 93 (1873).

<sup>22</sup> Rüdüsile, A.: *Nachweis, Bestimmung und Trennung der chemischen Elemente*, vol. 4 (1916), p. 445. Akademische Buchhandlung von Max Drechsel, Bern.

<sup>23</sup> Baskerville, C.: *J. Am. Chem. Soc.*, 16, 427 (1894).

<sup>24</sup> Berthier, P.: *Ann. chim. phys.*, (3) 7, 74 (1843).

<sup>25</sup> Gooch, F. A.: *loc. cit.*, *ref.* 6.

- <sup>26</sup> Thornton, W. M., Jr.: loc. cit., p. 174, *ref.* 16.  
<sup>27</sup> Prepared by acting on potassium fluotitanate with sulfuric acid.  
<sup>28</sup> Stromeyer, A.: *Ann.*, 113, 127 (1860).  
<sup>29</sup> Chancel, G.: *Compt. rend.*, 46, 987 (1858).  
<sup>30</sup> Hess, W. H., and Campbell, E. D.: *J. Am. Chem. Soc.*, 21, 776 (1899).  
<sup>31</sup> Allen, E. T.: *ibid.*, 25, 421 (1903).  
<sup>32</sup> Hillebrand, W. F.: *U. S. Geol. Survey, Bull.* 700, 128 (1919).  
<sup>33</sup> This is made by adding a saturated aqueous solution of sulfurous acid to a few cubic centimeters of phenylhydrazine until the salt, which first crystallizes out, is redissolved to a yellow solution. If, after a few minutes, it exhales an odor of sulfur dioxide, this excess is neutralized with a drop or so of phenylhydrazine. This solution will keep indefinitely in a tightly stoppered bottle. To prepare the washing fluid, 5 to 10 cc. of the strong phenylhydrazine bisulfite solution is added to every 100 cc. of water.  
<sup>34</sup> Private communication from Dr. E. T. Allen, Dec. 10, 1914.  
<sup>35</sup> Gooch, F. A.: loc. cit., 436, *ref.* 6.  
<sup>36</sup> Ibbotson, F.: *The Chemical Analysis of Steel-Works' Materials*, 1920, p. 4. Longmans, Green and Co.  
<sup>37</sup> Thornton, W. M., Jr., and Hayden, E. M., Jr.: *Am. J. Sci.*, (4) 38, 137 (1914).  
<sup>38</sup> The ratio by weight of potassium oxide to zirconium oxide was nearly 25 to 1.  
<sup>39</sup> Lundell, G. E. F., and Knowles, H. B.: loc. cit., p. 347, *ref.* 17.  
<sup>40</sup> See Brown, J.: *J. Am. Chem. Soc.*, 39, 2358 (1917).  
<sup>41</sup> One hundred cc. of water dissolves 0.241 gram at 0° C. and 0.222 gram at 100° C. of hydrated calcium sulfate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .  
<sup>42</sup> Fresenius, R.: *Z. anal. Chem.*, 50, 35 (1911).  
<sup>43</sup> Hess, W. H., and Campbell, E. D.: loc. cit., *ref.* 30.  
<sup>44</sup> Curtman, L. J., and Dubin, H.: *J. Am. Chem. Soc.*, 34, 1485 (1912).  
<sup>45</sup> See Thornton, W. M., Jr.: *Dissertation*, New Haven, 1914, p. 47 *et seq.*  
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## CHAPTER VII

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## CHAPTER VIII

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- <sup>14</sup> Van Brunt, C.: J. Am. Chem. Soc., 36, 1426 (1914).
- <sup>15</sup> Jones, C.: Trans. Am. Inst. Mining Eng., 17, 414 (1889).
- <sup>16</sup> Hillebrand, W. F.: loc. cit., p. 169, *ref.* 8.
- <sup>17</sup> Lundell, G. E. F., and Knowles, H. B.: J. Am. Chem. Soc., 45, 2620 (1923).
- <sup>18</sup> On the permanency of permanganate solutions see Morse, H. N., Hopkins, A. J., and Walker, M. S.: Am. Chem. J., 18, 401 (1896).
- <sup>19</sup> Gooch, F. A.: Proc. Am. Acad. Arts Sci., 13, 342 (1878).
- <sup>20</sup> Blum, W.: J. Am. Chem. Soc., 34, 1379 (1912).
- <sup>21</sup> Anon.: Bur. Standards, Circ. 40, 1-13 (1913).
- <sup>22</sup> McBride, R. S.: J. Am. Chem. Soc., 34, 393 (1912).
- <sup>23</sup> Besides the end-point correction, the burette should be tested for calibration errors (Osborne, N. S., and Veazey, B. H.: Bull. Bur. Standards, 4, 553, 1908) and the titer adjusted to the standard temperature 20° C. (Anon.: Bur. Standards, Circ. 19, 50, 1916).
- <sup>24</sup> Randall, D. L.: Am. J. Sci., (4) 24, 313 (1907).
- <sup>25</sup> Lundell, G. E. F., and Knowles, H. B.: loc. cit., p. 2621, *ref.* 17; Anon.: Proc. Am. Soc. Testing Materials, 24, I, 863 (1924).
- <sup>26</sup> Ingot iron of The American Rolling Mill Co., Middletown, Ohio, is excellent for the purpose.
- <sup>27</sup> Blair, A. A.: The Chemical Analysis of Iron, 1918, pp. 88 and 92. J. B. Lippincott Company.
- <sup>28</sup> Twenty-five cc. of ferric sulfate solution containing 2% of iron is a satisfactory amount for 0.125 gram of titanium dioxide.
- <sup>29</sup> In this way too the end-point error is automatically corrected.
- <sup>30</sup> Roman numerals designate the valence of the element after passage of the solution through the reductor.
- <sup>31</sup> A reduced uranium solution on being vigorously agitated in contact with air undergoes definite reoxidation to the quadrivalent state (Lundell, G. E. F., and Knowles, H. B.: J. Am. Chem. Soc., 47, 2637, 1925).
- <sup>32</sup> Van Brunt, C.: loc. cit., p. 1428, *ref.* 14.
- <sup>33</sup> Treadwell, W. D. (with Lüthy, M., and Rheiner, A.): Helvetica Chim. Acta, 4, 551 (1921); (with Blumenthal, M.): *ibid.*, 5, 732 (1922); (with Hristie, P., Egger, L., and Sturzenegger, P.): *ibid.*, 5, 806 (1922).
- <sup>34</sup> Nakazono, T.: J. Chem. Soc. Japan, 42, 526 (1921).
- <sup>35</sup> Kikuchi, S.: *ibid.*, 43, 173, 544 (1922); Kano, N.: *ibid.*, 43, 333, 550 (1922); 44, 37, 47 (1923); Hakomori, S.: *ibid.*, 43, 734 (1922).
- <sup>36</sup> A sketch of the apparatus is given in C. A., 16, 1543 (1922).
- <sup>37</sup> Knecht, E., and Hibbert, E.: Ber., 36, 1549 (1903).
- <sup>38</sup> Knecht, E., and Hibbert, E.: New Reduction Methods in Volumetric Analysis, 1918, pp. 11 and 51. Longmans, Green and Co.; *ibid.*, 1925, pp. 10 and 70.
- <sup>39</sup> Gallo, G.: Atti accad. Lincei, (5) 16, I, 325 (1907).
- <sup>40</sup> Hinrichsen, F. W.: Chem.-Ztg., 31, 738 (1907).
- <sup>41</sup> Ball, T. R., and Smith, G. MCP.: J. Am. Chem. Soc., 36, 1838 (1914).
- <sup>42</sup> See sketch of apparatus in original article.
- <sup>43</sup> Morley, A. M., and Wood, J. K.: J. Chem. Soc., 125, 518 (1924).
- <sup>44</sup> Shimer, P. W., and Shimer, E. B.: loc. cit., *ref.* 13.
- <sup>45</sup> Private communication from Mr. L. E. Barton of the Titanium Alloy Manufacturing Co., Sept. 18, 1914.
- <sup>46</sup> The dimensions of L. E. Barton's reductor have since been increased to

- 4.1 cm. by 55.9 cm. Cf. Scott, W. W.: Standard Methods of Chemical Analysis, 1922, p. 544. D. Van Nostrand Company.
- <sup>47</sup> Mr. C. E. Willoughby, working in the Johns Hopkins Chemical Laboratory, obtained excellent results in reducing 0.125 gram of titanous oxide with the reductor shown in Figure 19 (1.9 cm. internal diameter and 35 cm. between the constriction and the bulb), using iron alum as preventive and titrating with permanganate.
- <sup>48</sup> Hickson, E. F., *et al.*: Proc. Am. Soc. Testing Materials, **24**, I, 451 (1924).
- <sup>49</sup> Hibbert, E.: J. Soc. Chem. Ind., **28**, 189 (1909).
- <sup>50</sup> Knecht, E.: J. Soc. Dyers Colourists, **21**, 9 (1905).
- <sup>51</sup> Knecht, E., and Hibbert, E.: New Reduction Methods in Volumetric Analysis, 1925, p. 64. Longmans, Green and Co.
- <sup>52</sup> Atack, F. W.: J. Soc. Dyers Colourists, **29**, 9 (1913).
- <sup>53</sup> Neumann, B., and Murphy, R. K.: Z. angew. Chem., **26**, 613 (1913).
- <sup>54</sup> Murphy, R. K.: Dissertation, Darmstadt, 1913, p. 41.
- <sup>55</sup> See Murphy, R. K.: loc. cit., p. 33, *ref.* 54.
- <sup>56</sup> Boller, W.: Dissertation, Zürich, 1915, p. 24.
- <sup>57</sup> Boller, W.: loc. cit., p. 20, *ref.* 56.
- <sup>58</sup> Kikuchi, S.: J. Chem. Soc. Japan, **43**, 544 (1922).
- <sup>59</sup> See Treadwell, F. P.: Analytical Chemistry (W. T. Hall's translation), vol. 2 (1924), pp. 517-20. John Wiley & Sons, Inc.
- <sup>60</sup> Edgar, G., and Kemp, A. R.: loc. cit., *ref.* 8.
- <sup>61</sup> McCay, LeR. W., and Anderson, W. T., Jr.: J. Am. Chem. Soc., **43**, 2372 (1921).
- <sup>62</sup> Gooch, F. A., and Newton, H. D.: Am. J. Sci., (4) **23**, 365 (1907).
- <sup>63</sup> Newton, H. D.: *ibid.*, (4) **25**, 343 (1908).
- <sup>64</sup> Brandt, L.: Chem.-Ztg., **42**, 433, 450 (1918).
- <sup>65</sup> Lundell, G. E. F., and Knowles, H. B.: J. Am. Chem. Soc., **43**, 1560 (1921).
- <sup>66</sup> See Treadwell, F. P.: loc. cit., *ref.* 59.
- <sup>67</sup> Cf. Fay, H.: An Advanced Course in Quantitative Analysis, 1917, p. 28. John Wiley & Sons, Inc.
- <sup>68</sup> Edgar, G., and Kemp, A. R.: loc. cit., p. 783, *ref.* 8.
- <sup>69</sup> McCay, LeR. W., and Anderson, W. T., Jr.: loc. cit., p. 2375, *ref.* 61.
- <sup>70</sup> A solution of titanous sulfate containing 10% of sulfuric acid by volume does not become turbid on long boiling.
- <sup>71</sup> To remove any extractive matter that might possibly reduce permanganate.
- <sup>72</sup> The carbon dioxide must be free from hydrogen sulfide and other reducing substances. G. E. F. Lundell and H. B. Knowles wash the gas with a sodium bicarbonate solution.
- <sup>73</sup> Gooch, F. A., and Newton, H. D.: loc. cit., *ref.* 62.
- <sup>74</sup> Gooch, F. A.: Methods in Chemical Analysis, 1912, p. 6. John Wiley & Sons.
- <sup>75</sup> Gooch, F. A., and Newton, H. D.: loc. cit., p. 366, *ref.* 62.
- <sup>76</sup> Newton, H. D.: loc. cit., *ref.* 63.
- <sup>77</sup> Brandt, L.: loc. cit., *ref.* 64.
- <sup>78</sup> Van Brunt, C.: loc. cit., p. 1428, *ref.* 14.
- <sup>79</sup> The electrically heated reductor of C. Van Brunt has no superiority over the simpler form (q.v.).
- <sup>80</sup> Bismuth trioxide converts divalent to trivalent chromium.

## CHAPTER IX

<sup>1</sup> For a more thorough treatment of specific gravity see Morse, H. N.: *Exercises in Quantitative Chemistry*, 1905, pp. 128-49. Ginn & Company; Hillebrand, W. F.: *U. S. Geol. Survey, Bull.* 700, 49-57 (1919); Olsen, J. C.: *Van Nostrand's Chemical Annual*, 1922, pp. 747-67. D. Van Nostrand Company.

<sup>2</sup> A large vacuum desiccator is well suited to the purpose.

<sup>3</sup> The density of water at different temperatures may be obtained from a table. See Anon.: *Bur. Standards, Circ.* 19, 43 (1916); Olsen, J. C.: *loc. cit.*, p. 629, *ref. 1*.

<sup>4</sup> On certain special manipulations to be used in taking the specific gravity of a powder see Hillebrand, W. F.: *loc. cit.*, p. 55, *ref. 1*.

<sup>5</sup> Concerning further refinements in the construction and use of the pycnometer see Johnston, J., and Adams, L. H.: *J. Am. Chem. Soc.*, 34, 563 (1912).

<sup>6</sup> Anon.: *Standards Am. Soc. Testing Materials*, (1924) 821.

<sup>7</sup> The Smeeth separating apparatus as well as the manner of using it is described by J. S. Diller in *U. S. Geol. Survey, Bull.* 150, 19 (1898). The ordinary style of separatory funnel, however, can be made to answer the purpose.

<sup>8</sup> A brief account of the heavy liquids is given by Moses, A. J., and Parsons, C. L.: *Elements of Mineralogy, Crystallography and Blowpipe Analysis*, 1907, p. 151. D. Van Nostrand Company. See also Diller, J. S.: *loc. cit.*, *ref. 7*.

<sup>9</sup> Retgers, J. W.: *Neues Jahr. Mineral. Geol.*, (1889) II, 185.

<sup>10</sup> Diller, J. S.: *loc. cit.*, p. 22, *ref. 7*.

<sup>11</sup> See especially Mellor, J. W.: *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 127. Charles Griffin and Company, Ltd.; Anon.: *Standards Am. Soc. Testing Materials*, (1924) 976.

<sup>12</sup> This process is known as "quartering."

<sup>13</sup> See Scott, W. W.: *Standard Methods of Chemical Analysis*, vol. 2 (1922), p. 1491 *et seq.* D. Van Nostrand Company.

<sup>14</sup> Washington, H. S.: *Manual of the Chemical Analysis of Rocks*, 1919, p. 64. John Wiley & Sons, Inc.

<sup>15</sup> This style of mortar may be purchased from Eimer & Amend, 3rd Ave. and 18-19th Sts., New York City. See Catalogue AA (1920) p. 375. It is much superior to the old Plattner mortar. The Ellis mortar, recommended by W. F. Hillebrand (*loc. cit.*, p. 58, *ref. 1*), is doubtless a satisfactory instrument.

<sup>16</sup> Procurable from B. F. Starr & Co., 211 Guilford Ave., Baltimore, Md.

<sup>17</sup> Cf. Bauer, O., and Deiss, E.: *The Sampling and Chemical Analysis of Iron and Steel* (W. T. Hall and R. S. Williams' translation), 1915, pp. 3-5 and 32-124. McGraw-Hill Book Company.

<sup>18</sup> Through the courtesy of Dr. William F. Meggers of the Bureau of Standards.

<sup>19</sup> Cf. Hillebrand, W. F.: *loc. cit.*, p. 41, *ref. 1*.

<sup>20</sup> Brush, G. J., and Penfield, S. L.: *Determinative Mineralogy*, 1907, p. 239 *et seq.* John Wiley & Sons.

<sup>21</sup> On the practical applications of spectroscopy see Meggers, W. F., Kiess, C. C., and Stimson, F. J.: *Bur. Standards, Sci. Papers* 18, 235-55 (1922).

<sup>22</sup> G. W. Sears, and L. Quill (*J. Am. Chem. Soc.*, 47, 922, 1925) prefer sodium pyrosulfate and state that at least 12.5 parts of it must be used for 1 part of the ore to secure complete solution.

<sup>23</sup> Blair, A. A.: *The Chemical Analysis of Iron*, 1918, p. 32. J. B. Lippincott Company.

- <sup>24</sup> Hillebrand, W. F.: J. Am. Chem. Soc., **24**, 368 (1902).
- <sup>25</sup> On the testing of volumetric apparatus see Osborne, N. S., and Veazey, B. H.: Bull. Bur. Standards, **4**, 553 (1908).
- <sup>26</sup> Instead of igniting the precipitate apart from the filter it is quite permissible to make the precipitation in the presence of macerated filter paper and then ignite in the ordinary manner. Cf. Allen, E. T., and Johnston, J.: J. Ind. Eng. Chem., **2**, 196 (1910).
- <sup>27</sup> Riban, J.: Bull. soc. chim., **28**, 241 (1877).
- <sup>28</sup> The iron value should be corrected for vanadium (p. 167).
- <sup>29</sup> Knecht, E., and Hibbert, E.: Ber., **36**, 1549 (1903).
- <sup>30</sup> See Blair, A. A.: loc. cit., p. 116, *ref. 23*; Blum, W.: J. Am. Chem. Soc., **34**, 1379 (1912); Cunningham, T. R., and Coltman, R. W.: Ind. Eng. Chem., **16**, 58 (1924).
- <sup>31</sup> The 2 in. perforated platinum cone, designed by F. A. Gooch (Proc. Am. Acad. Arts Sci., **13**, 342, 1898), is a very satisfactory support for the asbestos, since it permits rapid filtration without loss of clarity and at the same time is slow to become clogged.
- <sup>32</sup> Hillebrand, W. F.: J. Am. Chem. Soc., **20**, 461 (1898).
- <sup>33</sup> R. W. Bunsen's method of separating the precipitate from the filter and burning the latter by itself is described by Treadwell, F. P.: Analytical Chemistry (W. T. Hall's translation), vol. 2 (1924), p. 32. John Wiley & Sons, Inc.
- <sup>34</sup> It is highly improbable that minerals of this type will contain either arsenic or molybdenum, but a little platinum is likely to be in the solution as the result of fusions made in platinum crucibles.
- <sup>35</sup> Quadrivalent vanadium is not sensitive to atmospheric oxidation; hence the deoxidized solution may be boiled in an open vessel with impunity.
- <sup>36</sup> Obtained preferably from a cylinder of the liquefied gas.
- <sup>37</sup> Cf. Hillebrand, W. F.: U. S. Geol. Survey, Bull. **700**, 186 (1919); Lundell, G. E. F., and Knowles, H. B.: J. Am. Chem. Soc., **43**, 1560 (1921).
- <sup>38</sup> Cf. Watson, T. L.: J. Wash. Acad. Sci., **2**, 431 (1912).
- <sup>39</sup> Hillebrand, W. F.: loc. cit., p. 187, *ref. 37*.
- <sup>40</sup> Hillebrand, W. F.: loc. cit., p. 188, *ref. 37*.
- <sup>41</sup> Newton, H. D.: Dissertation, New Haven, 1908.
- <sup>42</sup> Cf. Travers, A.: Compt. rend., **166**, 289 (1918); Tomiček, O.: Rec. trav. chim., **43**, 786 (1924).
- <sup>43</sup> Hess, F. L., and Wells, R. C.: Am. J. Sci., (4) **31**, 432 (1911).
- <sup>44</sup> Giles, W. B.: Chem. News, **99**, 27 (1909).
- <sup>45</sup> Marignac, C.: Ann. chim. phys., (4) **13**, 23 (1868).
- <sup>46</sup> Private communication from Prof. F. W. Clarke of the U. S. Geological Survey, May 1, 1911.
- <sup>47</sup> Private communication from Dr. Roger C. Wells of the U. S. Geological Survey, May 8, 1911.
- <sup>48</sup> Noyes, A. A., and Bray, W. C.: Tech. Quart., **19**, 235 (1906).
- <sup>49</sup> This is of doubtful necessity, since potassium pyrosulfate is an oxidizing flux.
- <sup>50</sup> Cf. Whiteford, G. H.: Dissertation, Baltimore, 1917, p. 11.
- <sup>51</sup> The washing solution is best prepared by neutralizing 20 cc. of c. p. nitric acid (sp. gr., 1.42) with pure ammonium hydroxide and diluting to 1000 cc.
- <sup>52</sup> The manganese in the precipitate is assumed to be present as the oxide,  $Mn_2O_4$ .
- <sup>53</sup> Walters, H. E.: Chem. News, **84**, 239 (1901).
- <sup>54</sup> Scott, W. W.: loc. cit., p. 552, *ref. 13*.

- <sup>55</sup> Murphy, R. K.: Dissertation, Darmstadt, 1913, p. 55.
- <sup>56</sup> Brown, J.: J. Am. Chem. Soc., 39, 2358 (1917).
- <sup>57</sup> Anon.: Bur. Standards, Circ. 26, 7 (1921).
- <sup>58</sup> Drown, T. M., and McKenna, A. G.: Trans. Am. Inst. Mining Eng., 20, 242 (1891).
- <sup>59</sup> For details see Washington, H. S.: loc. cit., p. 239, *ref. 14*.
- <sup>60</sup> Walters, H. E.: loc. cit., *ref. 53*.
- <sup>61</sup> For further details on the colorimetric determination of manganese see Washington, H. S.: loc. cit., pp. 51 and 220, *ref. 14*.
- <sup>62</sup> Epperson, A. W.: Ind. Eng. Chem., 17, 744 (1925).
- <sup>63</sup> Mitscherlich, A.: J. prakt. Chem., 81, 108 (1860); 83, 455 (1861).
- <sup>64</sup> Cooke, J. P., Jr.: Am. J. Sci., (2) 44, 347 (1867).
- <sup>65</sup> Thornton, W. M., Jr.: Dissertation, New Haven, 1914, p. 11.
- <sup>66</sup> Treadwell, F. P.: loc. cit., p. 432, *ref. 33*; Barnebey, O. L.: J. Am. Chem. Soc., 37, 1481, 1829 (1915).
- <sup>67</sup> Pratt, J. H.: Am. J. Sci., (3) 48, 149 (1894).
- <sup>68</sup> Cf. Hillebrand, W. F.: loc. cit., p. 189, *ref. 37*.
- <sup>69</sup> Mauzelius, R.: Sveriges Geol. Undersökning, Arsbok I, No. 3, 1907. See also Hillebrand, W. F.: J. Am. Chem. Soc., 30, 1120 (1908).
- <sup>70</sup> Gage, R. B.: *ibid.*, 31, 381 (1909).
- <sup>71</sup> A somewhat smaller crucible may be used. H. S. Washington (loc. cit., p. 186, *ref. 14*) employs one of only 35 cc. capacity.
- <sup>72</sup> Hydrofluoric acid may be conveniently measured in and poured from a "neocraft" graduate (distributed by the Emil Greiner Co., 55 Vandam St., New York City).
- <sup>73</sup> Barnebey, O. L.: loc. cit., p. 1489, *ref. 66*.
- <sup>74</sup> Hillebrand, W. F.: U. S. Geol. Survey, Bull. 700, 201 (1919).
- <sup>75</sup> W. F. Hillebrand (loc. cit., p. 184, *ref. 74*) considers that the vanadium in silicate minerals is in the trivalent condition. With oxide minerals, however, there is little or no ground on which to base an opinion.
- <sup>76</sup> Hackl, O.: Chem.-Ztg., 43, 9 (1919); Z. anal. Chem., 66, 401 (1925); 67, 197 (1925).
- <sup>77</sup> On the composition and properties of palau see Gurevich, L. J., and Wichers, E.: J. Ind. Eng. Chem., 11, 570 (1919).
- <sup>78</sup> Pope, F. J.: Trans. Am. Inst. Mining Eng., 29, 372 (1899).
- <sup>79</sup> The vanadium in iron ores increases with the titanium content.
- <sup>80</sup> Smith, J. L.: Am. J. Sci., (3) 1, 269 (1871); Hillebrand, W. F.: loc. cit., p. 207, *ref. 74*; Washington, H. S.: loc. cit., p. 191, *ref. 14*.
- <sup>81</sup> Whiteford, G. H.: loc. cit., p. 16, *ref. 50*.
- <sup>82</sup> Penfield, S. L.: Am. J. Sci., (3) 48, 31 (1894); Washington, H. S.: loc. cit., p. 210, *ref. 14*.
- <sup>83</sup> Gooch, F. A.: Am. Chem. J., 2, 247 (1880).
- <sup>84</sup> A thorough treatment of the determination of water in minerals is given by Hillebrand, W. F.: loc. cit., pp. 64-89, *ref. 74*.
- <sup>85</sup> Shimer, P. W., and Shimer, E. B.: Orig. Com. 8th Intern. Congr. Appl. Chem., 1, 445 (1912).
- <sup>86</sup> Hagmaier, E. W.: Met. Chem. Eng., 16, 588 (1917).
- <sup>87</sup> Schoeller, W. R., and Powell, A. R.: The Analysis of Minerals and Ores of the Rarer Elements, 1919, pp. 98-9. Charles Griffin and Company, Ltd.
- <sup>88</sup> Knecht, E., and Hibbert, E.: New Reduction Methods in Volumetric Analysis, 1925, p. 72. Longmans, Green and Co.; Hibbert, E.: J. Soc. Chem. Ind., 28, 189 (1909).

- <sup>89</sup> Knecht, E., and Hibbert, E.: *loc. cit.*, pp. 10 and 68, *ref. 88*; Thornton, W. M., Jr., and Chapman, J. E.: *J. Am. Chem. Soc.*, **43**, 91 (1921); Thornton, W. M., Jr., and Wood, A. E.: *Ind. Eng. Chem.*, **19**, 150 (1927).
- <sup>90</sup> Blair, A. A.: *loc. cit.*, pp. 76, 80, 172, 256 and 259, *ref. 23*.
- <sup>91</sup> Precipitation of titanium by ammonium phosphate and by cupferron in the presence of phosphoric acid constitute exceptions.
- <sup>92</sup> Pattinson, J., and Pattinson, H. S.: *J. Soc. Chem. Ind.*, **14**, 443 (1895).
- <sup>93</sup> Blair, A. A.: Tenth Census U. S., **15**, 512 (1880).
- <sup>94</sup> Arnold, J. O.: *Steel Works Analysis*, 1895, p. 259. Whittaker and Co.
- <sup>95</sup> Blair, A. A.: *The Chemical Analysis of Iron*, 1918, pp. 76, 80, 172, 256 and 259. J. B. Lippincott Company.
- <sup>96</sup> The decomposition and evaporation should be carried out in a porcelain or Pyrex glass basin, since ferric chloride attacks platinum.
- <sup>97</sup> Hillebrand, W. F., and Lundell, G. E. F.: *J. Am. Chem. Soc.*, **42**, 2609 (1920).
- <sup>98</sup> Cf. Lundell, G. E. F., and Hoffman, J. I.: *Ind. Eng. Chem.*, **15**, 44 (1923).
- <sup>99</sup> Made by saturating ammonia water (sp. gr. 0.90) with sulfur dioxide.
- <sup>100</sup> Blair, A. A.: *loc. cit.*, pp. 76 and 80, *ref. 95*.
- <sup>101</sup> Pattinson, J., and Pattinson, H. S.: *loc. cit.*, *ref. 92*.
- <sup>102</sup> G. E. F. Lundell and J. I. Hoffman (*loc. cit.*, p. 44, *ref. 98*) state that at least a 5-fold excess of aluminum, or a 10-fold excess of iron, is necessary for the complete precipitation of phosphorus and that the ammonium hydroxide must be used only in very slight excess.
- <sup>103</sup> Ridsdale, N. D.: *Chem. News*, **120**, 219 (1920).
- <sup>104</sup> See Blair, A. A.: *loc. cit.*, p. 77, *ref. 95*.
- <sup>105</sup> The reagent is prepared by pouring 13 cc. of ammonium molybdate (150 grams per liter) into 10 cc. of nitric acid (sp. gr., 1.42).
- <sup>106</sup> Ridsdale, N. D.: *Proc. Cleveland Inst. Eng.*, **55**, 162 (1919).
- <sup>107</sup> Baskerville, C.: *J. Anal. Appl. Chem.*, **7**, 194 (1894).
- <sup>108</sup> Sodium nitrate would be better, since sodium titanate is less soluble than potassium titanate. Cf. Auger, V.: *Compt. rend.*, **177**, 1302 (1923).
- <sup>109</sup> See Blair, A. A.: *loc. cit.*, p. 100, *ref. 95*.
- <sup>110</sup> Cf. Camp, J. M.: *The Methods of the U. S. Steel Corporation for the Commercial Sampling and Analysis of Iron Ores*, 1914, p. 35. Carnegie Steel Company, Pittsburgh, Pa.
- <sup>111</sup> This recipe is practically the same as A. A. Blair's (*loc. cit.*, p. 92, *ref. 95*).
- <sup>112</sup> Ibbotson, F.: *The Chemical Analysis of Steel-Works' Materials*, 1920, p. 225. Longmans, Green and Co.
- <sup>113</sup> Hillebrand, W. F.: *U. S. Geol. Survey, Bull.* **700**, 35 (1919).
- <sup>114</sup> Camp, J. M.: *loc. cit.*, p. 50, *ref. 110*.
- <sup>115</sup> Blair, A. A.: *loc. cit.*, pp. 20 and 254, *ref. 95*.
- <sup>116</sup> Waddell, J.: *Analyst*, **44**, 307 (1919).
- <sup>117</sup> Moore, R. B., *et al.*: *Bur. Mines, Bull.* **212**, 283, 302 (1923).
- <sup>118</sup> Barnebey, O. L., and Isham, R. M.: *J. Am. Chem. Soc.*, **32**, 957 (1910).
- <sup>119</sup> Jamieson, G. S., and Wrenshall, R.: *J. Ind. Eng. Chem.*, **6**, 203 (1914).
- <sup>120</sup> Private communication from Mr. R. B. Williams of the Metal and Thermit Corporation, May 12, 1925.
- <sup>121</sup> Ledebur, A.: *Leitfaden für Eisenhütten-Laboratorien*, 1925, p. 49. Friedr. Vieweg & Sohn Akt.-Ges., Braunschweig. See also Waterhouse, G. B.: *Chem. Eng.*, **7**, 198 (1907).
- <sup>122</sup> Ledebur, A.: *loc. cit.*, pp. 49-52, *ref. 121*.

- <sup>123</sup> Smith, J. L.: *Am. J. Sci.*, (2) 10, 354 (1850); *Original Researches in Mineralogy and Chemistry*, 1884, p. 108. Printed for presentation only.
- <sup>124</sup> Wells, H. L.: *Introduction to Volumetric Analysis and Combustions*, 1916, p. 7. Sheffield Scientific School of Yale University.
- <sup>125</sup> Complete reduction of both the titanium and iron is secured by the addition of 10 grams of granulated zinc and an extra 15 cc. of concentrated sulfuric acid.
- <sup>126</sup> Murphy, R. K.: *loc. cit.*, pp. 41 and 52, *ref. 55*.
- <sup>127</sup> Cf. Bornemann, K., and Schirmeister, H.: *Metallurgie*, 7, 711 (1910).
- <sup>128</sup> The loss in weight does not represent all of the silicon dioxide, an additional quantity being recovered from an aliquot part of the solution.
- <sup>129</sup> The author is inclined to doubt the validity of this assumption.
- <sup>130</sup> The methylene blue process for estimating titanium is featured in Lunge, G.: *Chemisch-technische Untersuchungsmethoden* (E. Berl's revision), vol. 2 (1922), pp. 162, 175 and 747. Julius Springer, Berlin.
- <sup>131</sup> Ball, T. R., and Smith, G. MCP.: *J. Am. Chem. Soc.*, 36, 1838 (1914).
- <sup>132</sup> Noyes, W. A.: *J. Anal. Appl. Chem.*, 5, 39 (1891).
- <sup>133</sup> Anderson, R. J.: *Bur. Mines, Reports of Investigations*, Ser. No. 2406, 5 (1922).
- <sup>134</sup> See analyses listed by G. P. Merrill in *Ann. Rept. U. S. Nat. Museum*, (1899) 230 and by F. W. Clarke in *U. S. Geol. Survey, Bull.* 770, 498 (1924).
- <sup>135</sup> Handy, J. O.: *J. Am. Chem. Soc.*, 18, 766 (1896).
- <sup>136</sup> Mellor, J. W.: *loc. cit.*, p. 446, *ref. 11*.
- <sup>137</sup> Lenher, V., and Crawford, W. G.: *J. Am. Chem. Soc.*, 35, 138 (1913).
- <sup>138</sup> Cf. Lunge, G.: *loc. cit.*, p. 571, *ref. 130*.
- <sup>139</sup> Private communication from Dr. J. Edward Whitfield of the firm of Booth, Garrett & Blair, Philadelphia, Pa., Apr. 30, 1926.
- <sup>140</sup> Lundell, G. E. F., and Knowles, H. B.: *J. Am. Chem. Soc.*, 42, 1439 (1920).
- <sup>141</sup> Moore, R. B., *et al.*: *loc. cit.*, p. 301, *ref. 117*.
- <sup>142</sup> If the filtrate from the ferrous sulfide, on being acidified and boiled, shows insoluble sulfides, it should be filtered before making the cupferron precipitation.
- <sup>143</sup> Hillebrand, W. F.: *loc. cit.*, pp. 176-7, *ref. 113*.
- <sup>144</sup> This does not represent all of the rare earths originally present in the ore, since the precipitation of these elements by cupferron from a solution containing 10% of sulfuric acid by volume is by no means complete. Cf. Lundell, G. E. F., and Knowles, H. B.: *J. Ind. Eng. Chem.*, 12, 344 (1920).
- <sup>145</sup> Brown, J.: *loc. cit.*, p. 2363, *ref. 56*.
- <sup>146</sup> See especially Travers, A.: *Chimie & industrie*, 2, 385 (1919); Powell, A. R., and Schoeller, W. R.: *Analyst*, 44, 397 (1919); Schoeller, W. R.: *J. Soc. Chem. Ind.*, 40, 127 (1921); Marden, J. W., and Rich, M. N.: *J. Ind. Eng. Chem.*, 12, 651 (1920); *Bur. Mines, Bull.* 186, 27, 67 (1921).
- <sup>147</sup> Cf. Washington, H. S.: *J. Wash. Acad. Sci.*, 11, 9 (1921).
- <sup>148</sup> If it is desired to co-precipitate the manganese with the other members of the ammonium hydroxide group, 1 gram of ammonium persulfate should be added prior to the neutralization. Cf. Epperson, A. W.: *loc. cit.*, p. 744, *ref. 62*.
- <sup>149</sup> Cf. Whiteford, G. H.: *loc. cit.*, p. 11, *ref. 50*.
- <sup>150</sup> Hillebrand, W. F.: *loc. cit.*, p. 164, *ref. 113*. The error caused by co-precipitation of vanadium is not likely to be of serious consequence. This comment applies also to titanium ores. Cf. Lundell, G. E. F., and Knowles, H. B.: *loc. cit.*, p. 347, *ref. 144*.
- <sup>151</sup> See especially Hillebrand, W. F.: *loc. cit.*, pp. 1-285, *ref. 113*; Mellor, J. W.: *loc. cit.*, pp. 1-778, *ref. 11*; Washington, H. S.: *Manual of the Chemical Analysis of Rocks*, 1919, pp. 1-271. John Wiley & Sons, Inc.

- <sup>152</sup> Hillebrand, W. F.: loc. cit., pp. 119 and 155, *ref. 113*.  
<sup>153</sup> Chatard, T. M.: Am. Chem. J., 13, 106 (1891).  
<sup>154</sup> Gooch, F. A.: Proc. Am. Acad. Arts Sci., n. s., 12, 435 (1885).  
<sup>155</sup> Hillebrand, W. F.: loc. cit., p. 179, *ref. 113*.  
<sup>156</sup> Mellor, J. W.: loc. cit., p. 200, *ref. 11*.  
<sup>157</sup> Rieke, R., and Betzel, R.: Arch. Phys. Chem. Glases Keram., 1, 45 (1912).  
<sup>158</sup> On the mineralogical composition of sands see Clarke, F. W.: loc. cit., p. 505, *ref. 134*.  
<sup>159</sup> Barrett, E. P.: Mining Sci. Press, 117, 729 (1918).  
<sup>160</sup> Doolittle, R. E., *et al.*: Official and Tentative Methods of Analysis, 1919, p. 309. Association of Official Agricultural Chemists.  
<sup>161</sup> Private communication from Prof. F. P. Dunnington, Sept. 27, 1917.  
<sup>162</sup> Cf. Geilmann: J. Landw., 68, 107 (1920).  
<sup>163</sup> Hillebrand, W. F.: loc. cit., pp. 255 and 271, *ref. 113*.  
<sup>164</sup> Epperson, A. W.: loc. cit., p. 744, *ref. 62*.  
<sup>165</sup> Schoeller, W. R., and Powell, A. R.: J. Chem. Soc., 119, 1927 (1921); Schoeller, W. R., and Waterhouse, E. F.: Analyst, 49, 215 (1924); Powell, A. R., and Schoeller, W. R.: *ibid.*, 50, 485 (1925).  
<sup>166</sup> Hess, F. L., and Wells, R. C.: loc. cit., *ref. 43*.  
<sup>167</sup> Hess, F. L., and Wells, R. C.: loc. cit., p. 440, *ref. 43*.  
<sup>168</sup> Walker, T. L., and Parsons, A. L.: Univ. Toronto Studies, Geol. Ser., No. 16, 14 (1923).  
<sup>169</sup> Headden, W. P.: Proc. Colo. Sci. Soc., 11, 188 (1917); Walker, T. L., and Parsons, A. L.: loc. cit., p. 34, *ref. 168*.  
<sup>170</sup> Todd, E. W.: Univ. Toronto Studies, Geol. Ser., No. 16, 40 (1923).  
<sup>171</sup> G. Chesneau (Compt. rend., 149, 1132, 1909) states that 1 gram of columbium or tantalum pentoxide produces the same color with hydrogen peroxide as 0.005 gram of titanite oxide.  
<sup>172</sup> Mar, F. W.: Am. J. Sci., (3) 40, 403 (1890).  
<sup>173</sup> Probably dysanallyte. See Dana, J. D.: System of Mineralogy, 1909, pp. 724 and 1082. John Wiley & Sons, Inc.  
<sup>174</sup> Hess, F. L., and Wells, R. C.: loc. cit., p. 435, *ref. 43*.  
<sup>175</sup> Hauser, O., and Herzfeld, H.: Zentr. Mineral., (1910) 759; Meyer, R. J., and Hauser, O.: Die Analyse der seltenen Erden und der Erdsäuren, 1912, p. 303. Ferdinand Enke, Stuttgart.  
<sup>176</sup> Schoeller, W. R., and Powell, A. R.: The Analysis of Minerals and Ores of the Rarer Elements, 1919, p. 129 *et seq.* Charles Griffin and Co., Ltd.  
<sup>177</sup> The Standard Pebble Phosphate (1923) of the Bureau of Soils contains 0.19% TiO<sub>2</sub>.  
<sup>178</sup> Rudnick, P., *et al.*: J. Ind. Eng. Chem., 7, 446 (1915). On the probable accuracy of this method see Lundell, G. E. F., and Knowles, H. B.: *ibid.*, 14, 1136 (1922); Lundell, G. E. F., and Hoffman, J. I.: J. Assoc. Official Agr. Chem., 8, 184 (1924).  
<sup>179</sup> Apatite has the formula Ca<sub>4</sub>(CaF)(PO<sub>4</sub>)<sub>3</sub>.  
<sup>180</sup> Watson, T. L., and Taber, S.: Va. Geol. Survey, Bull. III-A, 104 (1913).  
<sup>181</sup> Penfield, S. L., and Foote, H. W.: Am. J. Sci., (4), 7, 97 (1899).  
<sup>182</sup> A correct determination of ferrous iron can be made in ilmenite-nelsonite but not in rutile-nelsonite.  
<sup>183</sup> Glaser, C.: J. Am. Chem. Soc., 18, 782 (1896).  
<sup>184</sup> Chesneau, G.: Compt. rend., 153, 429 (1911).  
<sup>185</sup> Robinson, W. O., Steinkoenig, L. A., and Miller, C. F.: U. S. Dep. Agr., Bull. 600, 17 (1917).



- <sup>186</sup> Hunter, M. A.: J. Am. Chem. Soc., 32, 330 (1910).  
<sup>187</sup> See Billy, M.: Ann. chim., 16, 5 (1921).  
<sup>188</sup> Mixer, W. G.: Am. J. Sci., (4) 27, 393 (1909).  
<sup>189</sup> Shimer, P. W., and Shimer, E. B.: loc. cit., p. 449, *ref. 85*.  
<sup>190</sup> Private communication from Dr. P. W. Shimer of the Shimer Chemical Co., Easton, Pa., Apr. 14, 1926.  
<sup>191</sup> Shimer, P. W.: Trans. Am. Inst. Mining Eng., 15, 455 (1886).  
<sup>192</sup> Shimer, P. W.: J. Ind. Eng. Chem., 1, 738 (1909).  
<sup>193</sup> For further information on the determination of graphite consult Blair, A. A.: loc. cit., p. 162, *ref. 95*.  
<sup>194</sup> Private communication from Mr. L. E. Barton of the Titanium Alloy Manufacturing Co., Mar. 6, 1924.  
<sup>195</sup> Alundum ware is manufactured by the Norton Co., Worcester, Mass.  
<sup>196</sup> It is not feasible to use a very much larger sample for the determination of titanium by the cupferron method owing to the bulky nature of the precipitates.  
<sup>197</sup> Thornton, W. M., Jr., and Hayden, E. M., Jr.: Am. J. Sci., (4) 38, 137 (1914).  
<sup>198</sup> Private communication from Mr. L. E. Barton, Mar. 6, 1924.  
<sup>199</sup> Ibbotson, F.: loc. cit., p. 214, *ref. 112*.  
<sup>200</sup> Johnson, C. M.: Rapid Methods for the Chemical Analysis of Special Steels, Steel-Making Alloys and Graphite, 1914, p. 51. John Wiley & Sons, Inc.  
<sup>201</sup> Fleming, W. R.: Iron Age, 93, 64 (1914); Fleming Combustion Apparatus, pp. 1-7. Eimer & Amend. See also Treadwell, F. P.: loc. cit., p. 350, *ref. 33*, in which the method used at the Bureau of Standards is described.  
<sup>202</sup> Private communication from Mr. L. E. Barton, May 19, 1926.  
<sup>203</sup> Cf. Lundell, G. E. F., and Hoffman, J. I.: Ind. Eng. Chem., 15, 171 (1923).  
<sup>204</sup> Anon.: Standards Am. Soc. Testing Materials, (1924) 275.  
<sup>205</sup> Johnson, C. M.: loc. cit., p. 53, *ref. 200*.  
<sup>206</sup> Ibbotson, F.: loc. cit., p. 215, *ref. 112*.  
<sup>207</sup> Five to 7 cc. of ammonia solution (sp. gr., 0.90) should be added in excess to guard against the formation of basic ferric sulfate (Treadwell, F. P.: loc. cit., p. 403, *ref. 33*).  
<sup>208</sup> Grandjean, C.: Chimie & industrie, 8, 46 (1922).  
<sup>209</sup> If the solution has a green color, a few drops of alcohol should be added to precipitate the manganese.  
<sup>210</sup> Private communication from Mr. L. E. Barton, Sept. 18, 1914.  
<sup>211</sup> Private communication from Mr. R. B. Williams, May 12, 1925.  
<sup>212</sup> Shimer, P. W., and Shimer, E. B.: Orig. Com. 8th Intern. Congr. Appl. Chem., 1, 445 (1912).  
<sup>213</sup> Private communication from Mr. R. B. Williams, May 12, 1925.  
<sup>214</sup> Private communication from Mr. R. B. Williams, May 12, 1925.  
<sup>215</sup> Hunt, A. E., Clapp, G. H., and Handy, J. O.: J. Anal. Appl. Chem., 6, 24 (1892).  
<sup>216</sup> Sodium hydroxide would be preferable, since sodium titanate is less soluble than potassium titanate. Cf. p. 181.  
<sup>217</sup> Five to 10% sulfuric acid by volume would be better.  
<sup>218</sup> Anger, E. M.: Trans. Am. Electrochem. Soc., 33, 227 (1918).  
<sup>219</sup> Burgess, G. K., and Woodward, R. W.: Bur. Standards Tech. Papers, No. 207, 123 (1922); Gillett, H. W., and Mack, E. L.: Trans. Am. Electrochem. Soc., 43, 231 (1923).  
<sup>220</sup> Gillett, H. W., and Mack, E. L.: loc. cit., *ref. 219*.

- <sup>221</sup> Réglade, A., Geloso, M., and Domont, G.: *Rev. d'artillerie*, **88**, 485 (1921).  
See also Ferguson, J. D.: *Eng. Mining J.*, **106**, 356 (1918).
- <sup>222</sup> Bachman, F. E.: *Year Book Am. Iron Steel Inst.*, (1914) 370.
- <sup>223</sup> Blair, A. A.: *loc. cit.*, pp. 76, 80 and 172, *ref.* 95.
- <sup>224</sup> Shimer, P. W., and Shimer, E. B.: *loc. cit.*, p. 450, *ref.* 212.
- <sup>225</sup> Anon.: *Bur. Standards, Circ.* **14**, 9 (1916); Treadwell, F. P.: *loc. cit.*, p. 122, *ref.* 33.
- <sup>226</sup> Private communication from Mr. L. E. Barton, Sept. 18, 1914. See also Scott, W. W.: *loc. cit.*, p. 547, *ref.* 13.
- <sup>227</sup> Scott, W. W.: *loc. cit.*, p. 549, *ref.* 13.
- <sup>228</sup> McCabe, C. R.: *J. Ind. Eng. Chem.*, **5**, 735, 872 (1913).
- <sup>229</sup> Lundell, G. E. F., and Knowles, H. B.: *J. Ind. Eng. Chem.*, **12**, 562 (1920).
- <sup>230</sup> The ethereal solution contains most of the molybdenum and may therefore be used for the qualitative determination of this constituent. Cf. Blair, A. A.: *J. Am. Chem. Soc.*, **30**, 1228 (1908). If present, and a quantitative estimation is desired, it is better to start with a fresh portion of the steel.
- <sup>231</sup> The sodium hydroxide should be free from carbonate and otherwise as pure as possible. It must be tested for substances precipitable by ammonium hydroxide, and, if found, appropriate corrections applied in the aluminum determination.
- <sup>232</sup> Cf. Lundell, G. E. F., and Hoffman, J. I.: *Ind. Eng. Chem.*, **15**, 45 (1923).
- <sup>233</sup> Blair, A. A.: *The Chemical Analysis of Iron*, 1918, p. 92. J. B. Lippincott Company.
- <sup>234</sup> The sulfide precipitate contains, in addition to ferrous sulfide, the greater part of any nickel, cobalt or manganese that may have been present in the steel; but it is preferable to determine these in separate portions of the material.
- <sup>235</sup> Private communication from Dr. J. Edward Whitfield, Apr. 30, 1926.
- <sup>236</sup> See Blair, A. A. (*loc. cit.*, p. 17, *ref.* 233) for a description of J. E. Whitfield's apparatus for the rapid evaporation of liquids without loss.
- <sup>237</sup> Should the slag contain phosphoric acid, this can be removed by fusing the first precipitate of titanous acid with sodium carbonate and leaching with hot water.
- <sup>238</sup> Anon.: *Standards Am. Soc. Testing Materials*, (1924) 752.
- <sup>239</sup> Anon.: *ibid.*, (1924) 756.
- <sup>240</sup> Schütte, O.: *Dissertation*, Berlin, 1899, p. 40.
- <sup>241</sup> Thornton, W. M., Jr.: *Am. J. Sci.*, (4) **37**, 173 (1914); Ferrari, F.: *Ann. chim. applicata*, **4**, 341 (1915).
- <sup>242</sup> Knecht, E., and Hibbert, E.: *loc. cit.*, p. 71, *ref.* 88.
- <sup>243</sup> Kolthoff, I. M., and Tomiček, O.: *Rec. trav. chim.*, **43**, 776 (1924).
- <sup>244</sup> Anon.: *Proc. Am. Soc. Testing Materials*, **24**, I, 859 (1924); U. S. Govt. Master Spec., No. **278**, 1-12 (1925).
- <sup>245</sup> On the measurement of hiding-power and brightness see Pfund, A. H.: *J. Franklin Inst.*, **188**, 675 (1919); **189**, 371 (1920).
- <sup>246</sup> Lundell, G. E. F., and Knowles, H. B.: *Ind. Eng. Chem.*, **16**, 723 (1924).
- <sup>247</sup> F. P. Dunnington's colorimeter (Fig. 16) may be used for the comparison.
- <sup>248</sup> Anon.: *Titanox Pigment*, 1922, p. 19. Titanium Pigment Co., Inc., Niagara Falls, N. Y.
- <sup>249</sup> Private communication from Mr. L. E. Barton of the Titanium Pigment Co., Inc., May 31, 1923.
- <sup>250</sup> Brown, W. J.: *Proc. Am. Soc. Testing Materials*, **24**, I, 444 (1924).
- <sup>251</sup> Lunge, G.: *loc. cit.*, vol. **4** (1924), p. 767, *ref.* 130.
- <sup>252</sup> The Norwegian pigment contains zinc oxide.

<sup>253</sup> Anon.: U. S. Govt. Master Spec., No. 278, 1-12 (1925); Bur. Standards, Circ. 215, 1-12 (1925).

<sup>254</sup> The extraction mixture consists of 10 parts of ordinary ether (by volume), 6 parts of benzene, 4 parts of methyl alcohol and 1 part of acetone.

<sup>255</sup> The aqueous solution of sodium hydroxide is made by dissolving 100 grams of the solid in water and diluting to 300 cc.

<sup>256</sup> The alcoholic solution of sodium hydroxide is prepared by dissolving about 22 grams of the pure solid in 1000 cc. of ethyl alcohol (95%). The solution is allowed to stand in a stoppered bottle, the clear liquid decanted into another bottle and the second container is in like manner kept tightly closed. This solution should be colorless or only slightly yellow at the time of use. It will keep colorless longer, if the alcohol be previously treated with sodium hydroxide (about 80 grams to 1000 cc.), kept at about 50° C. for 15 days and then distilled.

<sup>257</sup> An Erlenmeyer flask with flanged neck and ground in stopper is convenient for the iodine test.

<sup>258</sup> The Hanus solution is made by dissolving 13.2 grams of iodine in 1000 cc. of 99.5% acetic acid and adding 3 cc. of bromine. See Scott, W. W.: loc. cit., pp. 1152 and 1167, *ref. 13*.

<sup>259</sup> Iodine number is centigrams of iodine to 1 gram of sample.

<sup>260</sup> Treadwell, F. P.: loc. cit., p. 551, *ref. 33*. On the stability of sodium thiosulfate solutions see Kilpatrick, M., Jr., and Kilpatrick, M. L.: J. Am. Chem. Soc., 45, 2132 (1923).

<sup>261</sup> Cf. Mar, F. W.: Am. J. Sci., (3) 41, 288 (1891).

<sup>262</sup> Zinc supplied by the Bureau of Standards (Standard Sample No. 43) contains less than 1 part of impurity in 10000.

<sup>263</sup> Anon.: U. S. Govt. Master Spec., No. 278, 1-12 (1925).

## CHAPTER X

<sup>1</sup> Cylinders of liquid ammonia may be obtained from the Goetz Ice Machine Co., 675 N. 12th St., Philadelphia, Pa.

<sup>2</sup> Allen, E. T., and Johnston, J.: J. Ind. Eng. Chem., 2, 196 (1910).

<sup>3</sup> Twenty per cent (sp. gr., 0.926) is a convenient concentration for most work.

<sup>4</sup> Bottles lined with paraffin are not satisfactory in hot weather; since the wax coating is very apt to loosen and expose the glass.

<sup>5</sup> Wohl, A.: Ber., 27, 1435 (1894).

<sup>6</sup> Baudisch, O.: Chem.-Ztg., 33, 1298 (1909); 35, 913 (1911); Baudisch, O., and King, V. L.: J. Ind. Eng. Chem., 3, 629 (1911).

<sup>7</sup> Phenylhydroxylamine is a skin poison; and, if spattered on the hands or face, it should be at once washed off with water and then with alcohol.

<sup>8</sup> The ammonium carbonate should be wrapped up in filter paper or porous cloth and the package tied with string.

<sup>9</sup> Marvel, C. S., and Kamm, O.: J. Am. Chem. Soc., 41, 276 (1919).

<sup>10</sup> Kasanof, D. R.: J. Ind. Eng. Chem., 12, 799 (1920).

<sup>11</sup> Slater, W. K.: J. Chem. Soc., 117, 587 (1920).

<sup>12</sup> A good grade of cupferron is supplied by the Eastman Kodak Co., Rochester, N. Y.

<sup>13</sup> Bellucci, I., and Grassi, L.: Gazz. chim. ital., 43, I, 570 (1913); Auger, V.:

Compt. rend., 170, 995 (1920); Auger, V., Lafontaine, L., and Caspar, C.: *ibid.*, 180, 376 (1925).

<sup>14</sup> Hillebrand, W. F.: U. S. Geol. Survey, Bull. 700, 46 (1919).

<sup>15</sup> Private communication from Mr. L. E. Barton of the Titanium Alloy Manufacturing Co., Sept. 18, 1914.

<sup>16</sup> See Merwin, H. E.: *Am. J. Sci.*, (4) 28, 119 (1909).

<sup>17</sup> Kilpatrick, M. L., Reiff, O. M., and Rice, F. O.: *J. Am. Chem. Soc.*, 48, 3019 (1926).

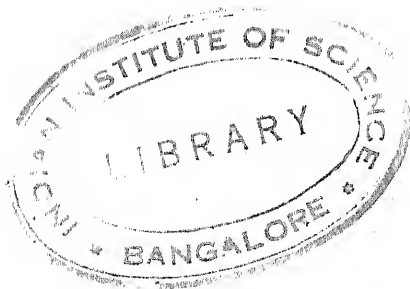
<sup>18</sup> Fenton, H. J. H.: *J. Chem. Soc.*, 65, 899 (1894).

<sup>19</sup> J. T. Baker Chemical Co., Phillipsburg, N. J.

<sup>20</sup> Lundell, G. E. F., and Knowles, H. B.: *Ind. Eng. Chem.*, 16, 723 (1924).

<sup>21</sup> Atack, F. W.: *J. Soc. Dyers Colourists*, 31, 183, 203 (1915).

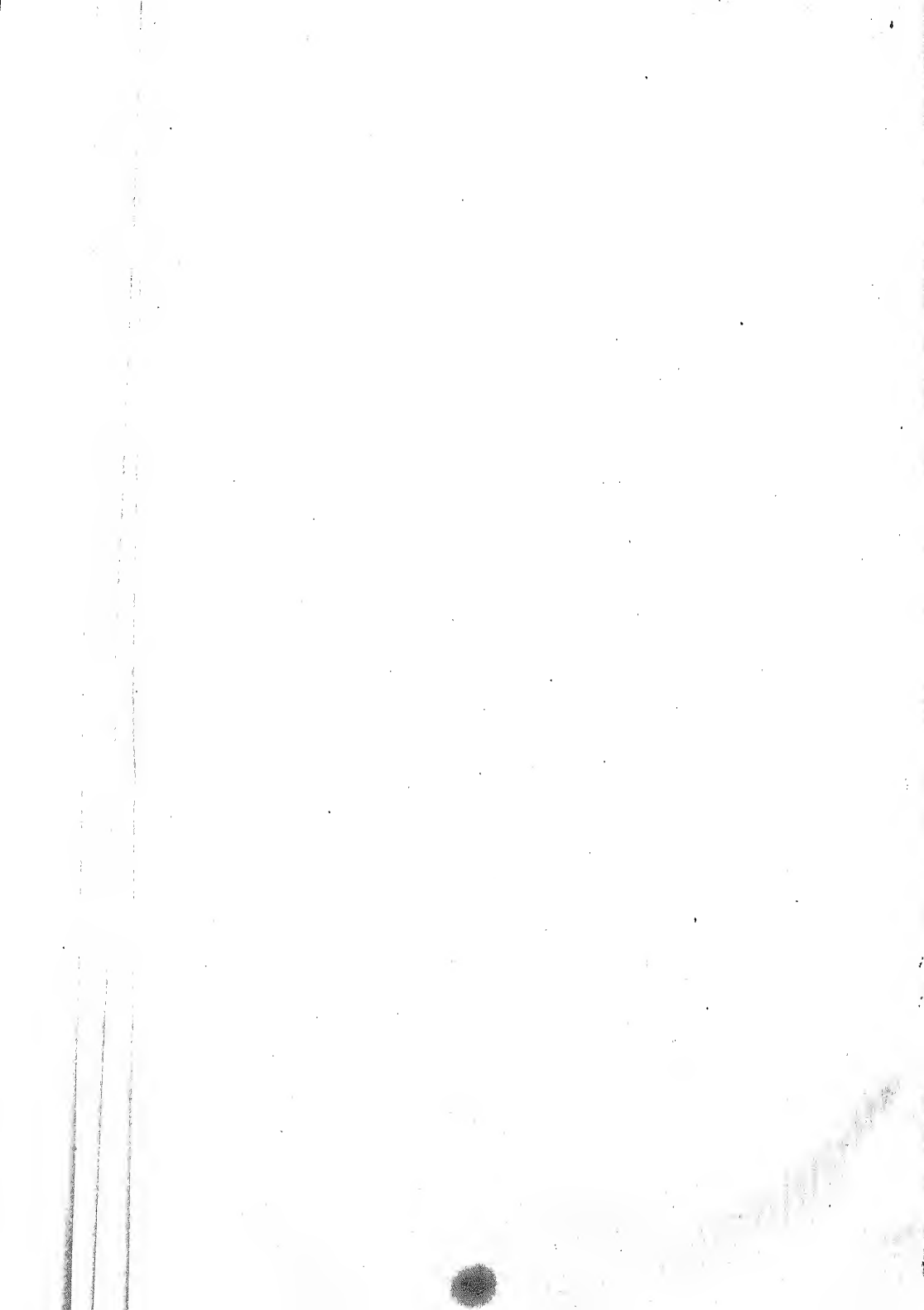
<sup>22</sup> Sulfur trioxide fumes rise quietly from the surface and do not bubble up through the liquid.

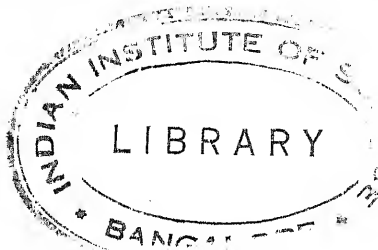


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